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

Amar Telidji University-Laghouat

FACULTY: TECHNOLOGY

DEPARTMENT: PROCESS ENGINEERING

MASTER THESIS

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DOMAIN: Science and Technology

FIELD: Process Engineering

OPTION: Materials Process Engineering

Theme:

Valorization of natural material for the removal of an industrial pollutant

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Promotion : JUNE 2024

Dedication

I always open my thanks to God Almighty, who helped me accomplish this memorandum. I dedicate the fruit of my efforts to the one whom God has endowed with prestige and dignity. To the one who taught me to give without waiting, my beloved father, may God protect him To my angel in life. To the meaning of love and tenderness. To the one whose prayers were the secret of my success and whose tenderness was the balm for my wounds, my dear mother, may God protect her. To my beloved teacher, Nasrallah Fadila, who was my role model, who gave and did not wait to give, I dedicate all my thanks and praise to her, may God bless her and make her happy wherever she lands.

I dedicate this humble work to the pure and tender heart and innocent soul, to my soul mate, my sister Khadija, to my dear uncle Youssef and his generous family, especially the little chick Ikhlas. To my dear brothers Taher, Ilyasse and Houssam, to all the Saoudi and Ben Messaoud families.
To my friend Farah Taher A companion who accompanied me on the road and became the best companion after the road. To my friends who were not born by my mother, companions on the path of life and part of me, each with her own name.

Asmaa

Dedication

To the dearest and closest people to my heart, to my dear mother and my dear father, who were my help and support, and whose blessed supplications had the greatest impact. In running the research ship until it docks in this way.

To my brothers and friends who encouraged me to complete this journey

To my teachers and my creditors who showered me with love and appreciation Advice, direction and guidance.

To all of them I dedicate this humble work; Asking God The Most High is destined to benefit us from it and provide us with its success.

Hadjer

Acknowledgements

Praise be to God who removes all praise Based on the principle that whoever does not thank people does not thank God,

We extend our sincere thanks and appreciation to the supervising professor, BOUDAOUD ASMA, *for her guidance and directions that she never skimped on us.*

We also extend our sincere thanks and benevolence to every hand that accompanied us in this work, whether from near or far,

And thanks are also extended to our guardians. Who ensured to provide us with all the appropriate conditions to accomplish this work

We also do not forget to thank all the professors and supervisors who provided us with a helping hand and we learned a lot from them.

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List of Abbreviations

Abbreviations	Designation
WP	Woodworking powder
MB	Methylene blue
C_0	Initial concentration of adsorbate
C_e	Equilibrium concentrations
V	Volume of solution
m	Mass of adsorbent
M	Molarity
Q	Adsorption capacity
R	removal efficiency
min	Minute
mg	Milligram
h	hour
λ max	Maximum wavelength
pH	Hydrogen potential
t	Time
T	Temperature
UV-vis	Ultraviolet-visible
Qe	Quantity adsorbed at equilibrium
K	Kelvin
K_L	Langmuir constant related to the rate of adsorption
K_F	Freundlich equation constant.
n	Freundlich equation coefficient.

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General Introduction

In recent centuries, man has faced a challenge that he must overcome, which is to satisfy his constantly increasing needs without harming himself and the environment in the short or long term. Indeed, with scientific and technological progress, industry has developed and humans have made practically everything, and at the same time sometimes produce toxic waste and pollution sources that pose a major threat to human health and the balance of ecosystems.

Water, which symbolizes life, and which is included in any industrial process, often They are contaminated with organic and inorganic pollutants, so they must be treated before being released into the natural environment. Among these pollutants we find dyes that are used in all areas of the food industry, paper industry, construction, and the automobile industry, especially in the textile industry. Dyes can be removed through various processes, namely coagulation, flocculation, sedimentation, filtration on membranes, adsorption, etc. The removal of dyes In aqueous solutions by adsorption on various solids, especially activated carbon, has been the subject of much work. But the increasing demand for adsorbents used in treatment processes has led to their costs becoming more and more high, which justifies research to prepare new, more economical adsorbents.

The waste of Woodworking constitutes an important source of industrial waste. In fact, this by-product is likely to be of commercial importance. It is therefore important to recover this waste. To this end, we were interested in using wood waste as an adsorbent. This work falls within this framework, as a contribution to the study of the removal of methylene blue dye, by adsorption on woodworking powder.

Our work is divided into three chapters:

The first chapter deals with generalities about water contamination and dyes, their compositions, classifications, and toxicities.

In the second chapter, we give the experimental protocol related to the preparation of woodworking powder and the dye adsorbat as will the experimental descrption of adsorption technique used in this work.

The third chapter is devoted to presenting and discussing the results obtained.

Finally, we ended the manuscript with a general conclusion related to the most important results reached by this study.

Chapter I:

Theoretical Aspect

I.1. Introduction

Water pollution is a global environmental issue that poses significant threats to ecosystems, human health, and economic development. Among the myriad of pollutants that contaminate our waterways, colored dyes stand out as a particularly concerning contributor. These dyes, widely used in various industries, are notorious for their ability to leach into water bodies, imparting hues that not only alter the appearance of the water, but also pose a range of ecological and human health risks.

I.2.Wastewater

Wastewater is a liquid with a heterogeneous composition of organic and mineral substances that are stuck or dissolved and may have a toxic property.

Wastewater is that water rich in dissolved and dissolved waste as a result of industrial or agricultural human activity, which flows in special sewage channels towards treatment plants.

Figure I.1: Wastewater

I.3. Source of wastewater

I.3.1. Polluted rainwater

Rainwater generally falls polluted due to pollutants in the air industrial areas are polluted to a strong degree in places with many chemical plants or when it falls on the ground, some of it falls on agricultural lands, some of it falls on roads and roofs of houses, and therefore it is a factor in the delivery of sand to drainage network [3].

Figure I.2: Polluted rainwater

I.3.2. Street water

Street water is discharged into the sewers and from there to the drainage network, carrying with it some sand and paper, which it drags in front of it in the roads.

Figure I.3: Street water

I.3.3. Industrial water

Industrial water includes waste water from different factories in the city, and it varies in its quantities from one factory to another, while we find the water used for cooling is almost free of impurities, and you also find that the waste resulting from the paper industry, for example, contains a very high concentration of dissolved suspended substances, organic or inorganic [4], and this water is different in nature from domestic water because it contains chemicals and toxic substances coming from factories, as well as laboratories and hospitals, this water releases unpleasant and toxic odors, especially at high temperatures.

Figure I.4: Industrial water

I.3.4. Domestic wastewater

Domestic wastewater it comes from various domestic uses of water and carries the characteristic of organic pollution and is divided into two parts:

1. Domestic water: is sourced from bathrooms kitchens and is generally rich in detergents, soap fats and other impurities.
2. Wastewater: which crosses the toilets and which is rich in various organic and azotic substances (urine ….) [5].

Figure I.5: Domestic water

I.4. Dyes

A dye is a chemical material capable of being fixed on a support, the more or less intense coloring of the different substances is linked to their chemical constitution. The first coloring materials were of vegetable origin (madder, indigo, gaude, campeche) or even animal (cochineal). At present, almost all of the coloring materials used are derivatives of the hydrocarbons contained in coal tar. The affinity of the dye for the fiber is particularly developed for dyes which have an accentuated acidic or basic character. These characteristics specific to organic dyes increase their persistence in the environment and make them unwilling to biodegrade [6].

1.4.1. Nature of the dyes

Dyes are colored chemical compounds, natural or synthetic, in general organic, which have the property of durably coloring the support on which they are applied under certain conditions. Modern industrial terminology defines a dye as a product containing the pure organic dye with different additives and cutting agents, which facilitate its use [7].

1.4.2. Chemical structure of dyes

Dyes are colored compounds that chemically bond to substrates during the dyeing process. Their structures vary depending on the type of dye, and they can be classified based on their chemical composition and application class and end-use. Here’s a brief overview of some common dye categories and their structural features [8]:

Table I.1: Dye classification.

Chemical classification	Tinctorial classification
Indigoid dyes	Acid or anionic dyes
Xanthene dyes	Developed or insoluble azo dyes
Phthalocyanines	Vat dyes
Anthraquinone	Direct dyes
Nitrated and nitrosated dyes	Mordant dyes
Azo dyes	Reactive dyes
Triphenylmethane dyes	Disperse dyes

a. Indigoid dyes

Take their name from the indigoid from which they are derived. Thus, the selenium, sulfur and oxygen counterparts of indigo blue are produce significant hypochromatic effects, with colors ranging from orange to turquoise [9]. Indigoid dyes are used as textile dyes, as additives in pharmaceuticals products, confectionery and medical diagnostics [10].

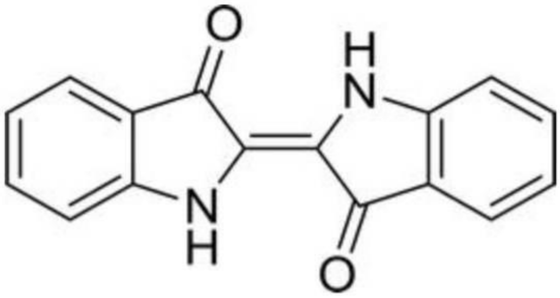

Figure I.6: Molecular structure of indigoid dyes

b. Xanthene dyes

Xanthene dyes are compounds derived from halogenated fluorescein. halogenated fluorescein. They fluoresce intensely. Their properties as markers in maritime accidents, or as flow tracers for rivers Underground is nevertheless well established. They are also used as colorants in food, cosmetics and textiles impression [9].

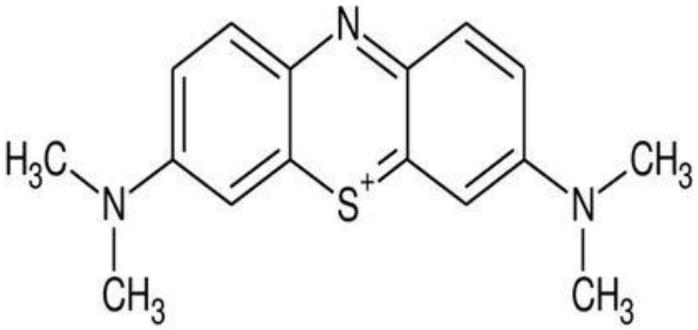

Figure I.7: Chemical structure of methylene bleu

c. Anthraquinone dyes

Dyes from a commercial point of view, anthraquinone dyes are the most important after azo dyes, after azo dyes. Their general formula is derived from anthracene, shows that the chromophore is a quinone nucleus to which hydroxyl or amino groups are added. Hydroxyl groups. These products are used to color polyester fibers, cellulose acetate and cellulose triacetate [9].

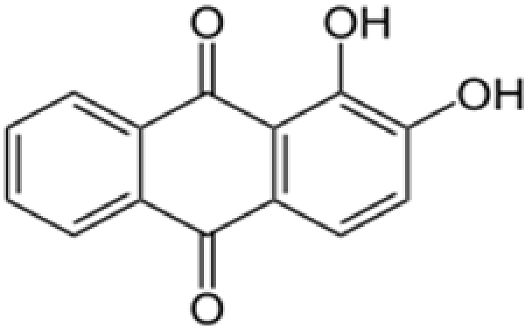

Figure I.8: Molecular structure of anthraquinone dyes

d. Nitrated and nitrosated dyes

These are a relatively old class of dyes, very limited in number. are still in use today, thanks to their low price and simple molecular structure. Structure, characterized by the presence of a nitro group (-NO2) in the ortho position of an electron-donor group (hydroxyl or amino groups) [9].

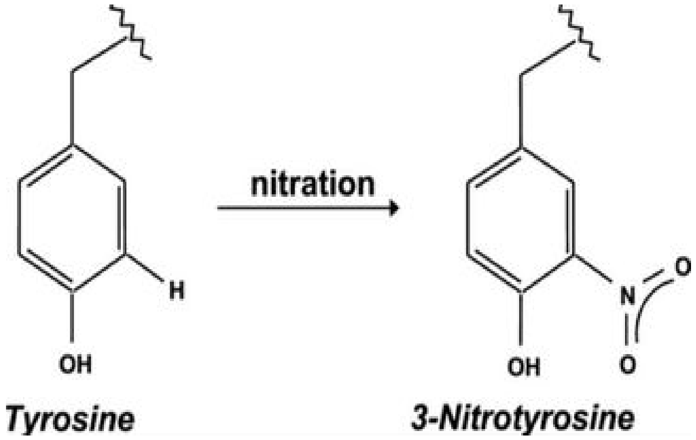

Figure I.9: Molecular structure of nitrated and nitrosated dyes

e. Phthalocyanines

These dyes have a complex structure based on the central copper atom. The dyes in this group are obtained by reacting dicyanobenzene in the presence of a metal halide (Cu, Ni, Co, Pt,…etc)[10].

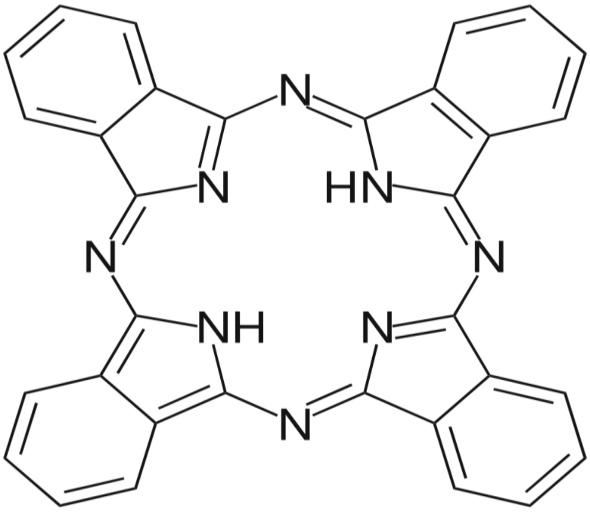

Figure I.10: Molecular structure of phthalocyanines dyes

f. Azo dyes

They are characterized by the presence within the molecule of an azo group (-N=N-) linking two benzene rings. This category of dyes is currently the most widespread application, accounting for over 50% of the world's colorant production [11].

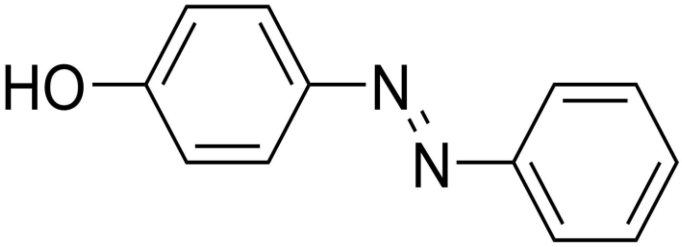

Figure I.11: Molecular structure of azo dyes

g. Triphenylmethane dyes

Triphenylmethane dyes and their heterocyclic derivatives are the oldest class of synthetic dyes. class of synthetic dyes. Although currently far less important than azo and anthraquinone azo and anthraquinone dyes, they have retained a certain commercial value, since they enable us to cover the entire range of shades [11].

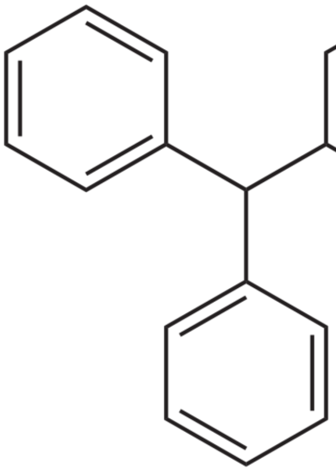

Figure I.12: Molecular structure of Triphenylmethane dyes

1.4.3. Impact on the health and environment

Toxicity of methylene blue: Toxicological data on the use of methylene blue in humans for many years indicate that there is no danger associated with the use of this product as a medicinal product, the total dose administered should not exceed 7 mg/kg. Methylene blue is not very dangerous, but it has a detrimental effect on living organisms and water.

a. Impact on human health

Extern al exposure: skin irritation and permanent damage to the eyes. By inhalation: rapid or difficult breathing and increased heart rate; Swallowed: irritation of the gastrointestinal tract, nausea, sweating, mental confusion, cyanosis and necrosis of human tissues [12].

b. Impact on the environment

Environmental toxicity several dyes are visible in water even at very low concentrations (1mg.l-1or less), their contribution to the pollution problems associated with the generation of a considerable amount of colored wastewater. These residual discharges into the ecosystem are a source of pollution, eutrophication and non-aesthetic disturbance in aquatic life [13].

1.5. Wastewater treatment technique

Wastewater treatment includes a range of important methods to purify contaminated water by removing organic and mineral solids before it can be reused or discharged[14]. These methods include:

Physical methods

- Precipitation methods (coagulation, flocculation, sedimentation).
- Reverse osmosis, filtration.
- Incineration.

Chemical methods

- Adsorption.
- Complexometric method.
- Ion exchange resin.

Biological methods

- Aerobic treatment.
- Anaerobic treatment[15].

1.4.1. Chemical precipitation

Chemical precipitation is a technique used in water and wastewater treatment to convert dissolved substances into solid particles for removal.it involves the addition of chemical to reduce the solubility of ionic components, especially metal cations, anions such as fluoride, cyanide and phosphate and organic molecules such as phenols and aromatic amines [16].

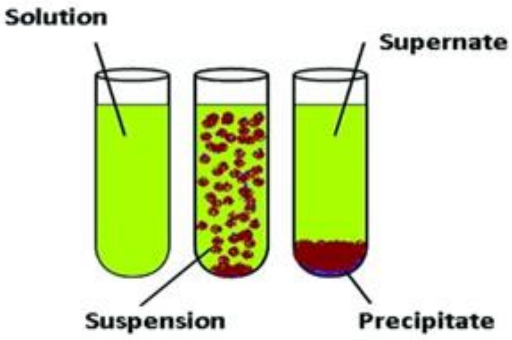

Figure I.13: Chemical precipitation.

1.4.2. Filtration

This process removes suspended substances in the aqueous medium is used directly in the case of clear water or after the agglomeration process of treated water, the thickness of the filter varies depending on the method used, where there is slow and fast filtration [17].

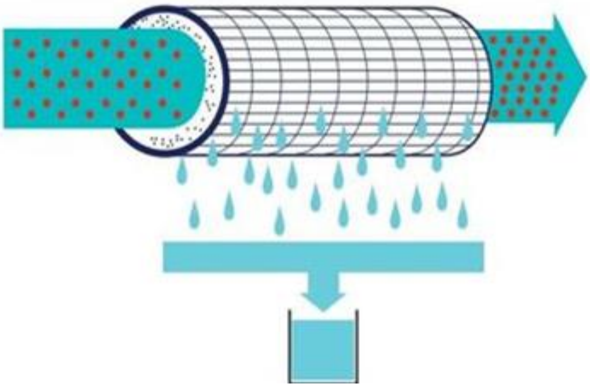

Figure I.14: Filtration.

1.5.3. Electrochemical Methods

All electrochemical methods are based on the interaction of electrical energy and matter. The measurements are done in an electrochemical cell where the sample and at least two electrodes are placed. The electrochemical cell possesses a large variety of concentration-dependent physical characteristics that may be exploited for chemical analysis. The methods are mainly used in analysis of aqueous samples but are also applicable to nonaqueous solutions and gases. In most of the methods one concentration-dependent electrical parameter, like voltage, current, resistance, or charge, is measured while the others are kept constant or manipulated to receive the desired response that correlates to the sample [18].

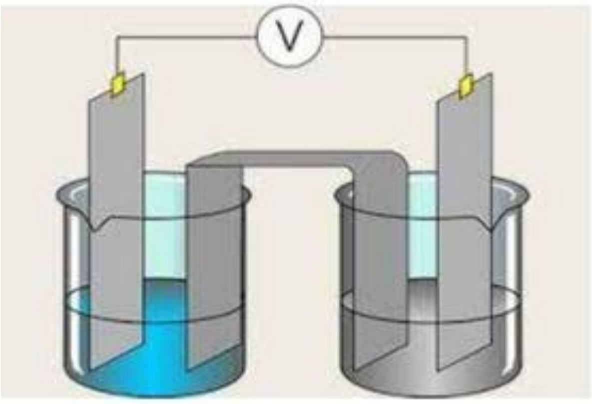

Figure I.15: Electrochemical methods.

I.4.5. Principle of liquid – liquid extraction

The principle of liquid-liquid extraction consists of making a mineral salt or acid soluble in an organic solvent, by complexing it with a compound having a hydrophilic group and hydrophobic radicals. The complexation process takes place at the interface between the two liquids brought into contact. The interface between the two phases is characterized by a high concentration of complexing agent molecules whose hydrophilic groups are soaked in the aqueous phase; a very polarized interfacial front is thus formed which has the effect of attracting the molecules (cations + anions) of salts or acids from the aqueous phase [19-20].

Liquid-liquid extraction is based on the distribution of solute M between the two immiscible aqueous and organic phases. During this transport, the chemical potential of the solute in the organic phase increases while that of the aqueous phase decreases. The equality of the chemical potential of a molecule in two phases in equilibrium results in the proportionality of the relative activities, therefore approximately in the proportionality of the concentrations of this molecule in the two phases [21].

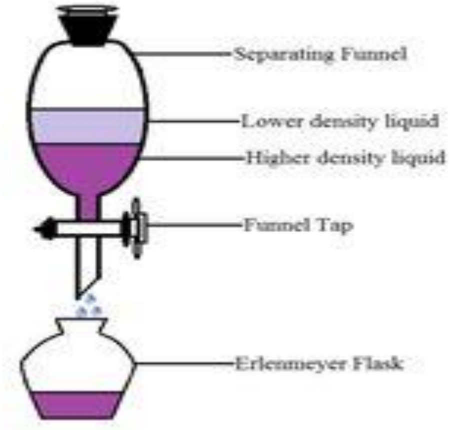

Figure.I.16: Extraction.

I.4.6. Biological Processes

Biological processes are those processes that are vital for an organism to live, and that shape its capacities for interacting with its environment. Biological processes are made of many chemical reactions or other events that are involved in the persistence and transformation of life forms Metabolism and homeostasis are examples [22].

Biological processes within an organism can also work as bioindicators. Scientists are able to look at an individual's biological processes to monitor the effects of environmental changes [23].

I.5. Adsorption

Adsorption is the process during which molecules of a fluid (gas or liquid) attach to the surface of a solid. The phase consisting of adsorbed molecules is called “solute” or “adsorbate” and the solid is called “adsorbent”. The surface of the solid includes the external and internal surfaces generated by the network of pores and cavities inside the adsorbent [24]. The adsorption process is one of the most widely used methods for the removal of pollutants. In addition, adsorption is a separation process by which certain components of a phase (liquid, gas) are fixed to the surface of a solid adsorbent by chemical or physical bonds. It is based on specific interactions (thermodynamics and kinetics) [25].

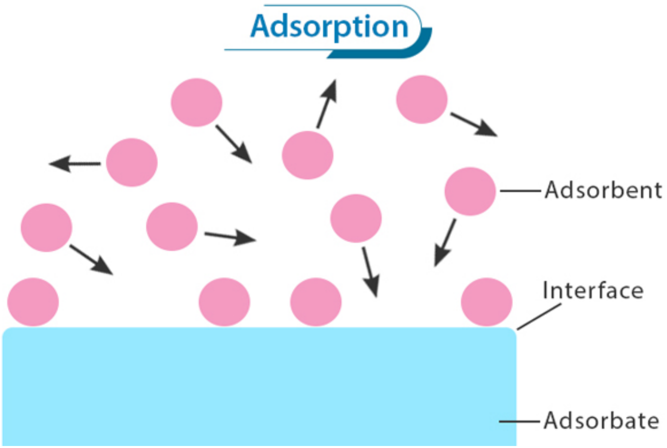

Figure.I.17: Adsorption process.

I.5.1. Types of adsorption

Depending on the importance of the energies involved between the adsorbent and the adsorbate, the forces responsible for the adsorption phenomenon can be of a physical or chemical nature, thus leading to two types of adsorption: physical adsorption “physisorption” and chemical adsorption “chemisorption”.

a. Physical adsorption

Physical adsorption or physisorption involves very weak interactions between molecular entities such as Van deer Waals forces of attraction and forces due to electrostatic polarization interactions; it is reversible and not very specific. Physical adsorption is rapid and generally limited by diffusion phenomena [26].

b. Chemical adsorption

Known as chemisorption, is an irreversible phenomenon due to a strong covalent chemical bond between the surface atoms of the solid and the adsorbed molecules. This type of adsorption involves high attraction energies, which lead to high heats of adsorption [26].

Table I.2: The difference between physical and chemical adsorption.

Property	Physical adsorption	Chemical adsorption
Heat of adsorption	On the order of 40kcal/mol	50-100 kcal / mol
Temperature	The yield is more appreciable at lower temperature than the boiling point of the adsorbent	Adsorption takes place even more temperature
Connection type	Van der Waals	Covalent , Ionic
Desorption	Easy	Difficult
Adsorption speed	Fast	Slow
Binding energies (kJ/mol)	<40	40
Saturation tap	Multilayer phenomenon	Monolayer phenomenon
Activation energy	No activation energy	Possibly involved
Type of substrate	Yield depends on the adsorbent more than the adsorbate	Depends on support and adsorbate (specific affinity)

I.5.2. Adsorption Mechanism

Adsorption mainly occurs in four stages. The figure represents a solid material (adsorbent) with the different areas in which the organic or inorganic molecules which are likely to interact with the solid

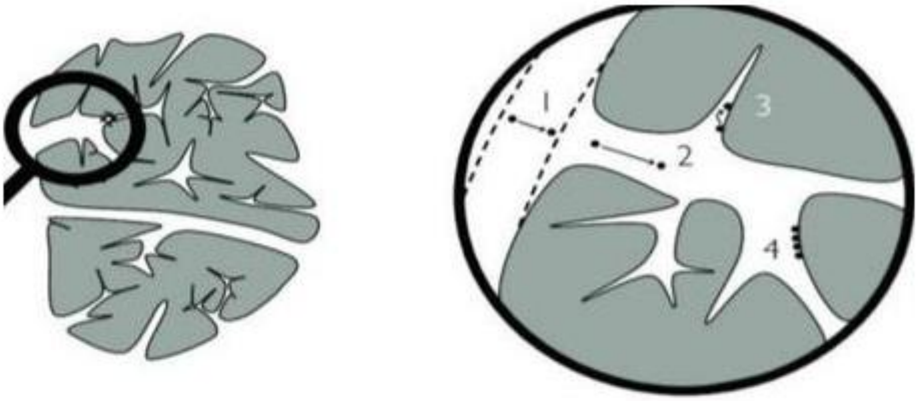

Figure I.18: Different stages of adsorption.

Before its adsorption, the solute will go through several stages [27]:

1. Diffusion of the adsorbate from the external liquid phase to that located at the vicinity of the surface of the adsorbent.
2. Extra granular diffusion of the material (transfer of solute through the liquid film towards the surface of the grains).
3. Intragranular transfer of material (transfer of material into the porous structure of the outer surface of the grains towards the active sites).
4. Adsorption reaction upon contact with the active sites, once adsorbed the molecule is considered immobile.

I.5.3. Adsorption isotherm

The shape of the isothermal curve varies according to the adsorbate-adsorbent pair studied. The adsorption isotherms for solutes with limited solubility have been classified by Giles 1974.

The system divides adsorption isotherms into four main classes: S, L (Langmuir), H (high affinity), and C (constant partition) classes, each representing distinct adsorption characteristics. [28]:

- The S class typically corresponds to isotherms with a steep initial slope, indicating strong adsorption at low concentrations .
- The L class, known as the Langmuir class, represents adsorption isotherms that follow the Langmuir model, showing a characteristic saturation at higher concentrations .
- The H class, or high affinity class, is associated with isotherms exhibiting high affinity for the adsorbate, leading to rapid adsorption at low concentrations. Lastly ,
- The C class, or constant partition class, includes isotherms where the adsorption process resembles the partitioning of solutes between immiscible solvents, showing a constant partition behavior.

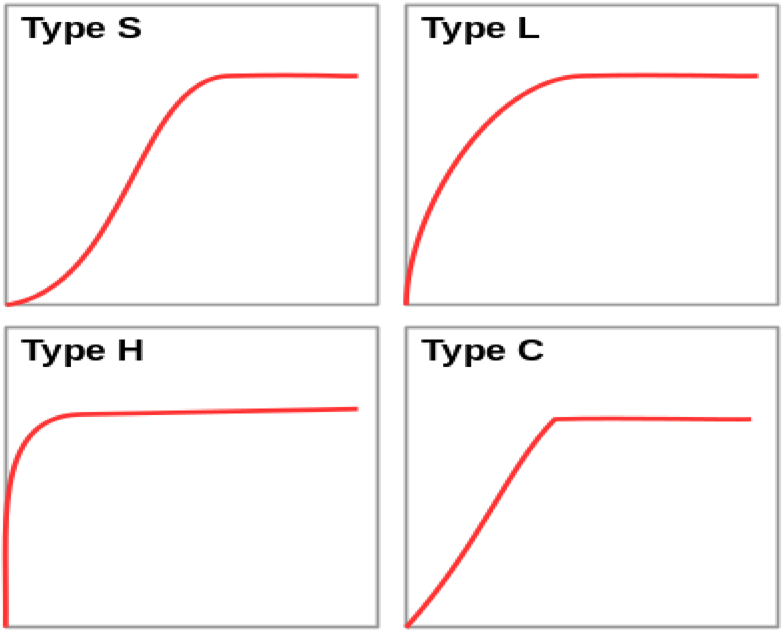

Figure I.19: The different types of adsorption isotherms.

I.5.4. Adsorption kinetics

Adsorption kinetics Knowledge of the adsorption equilibrium parameters makes it possible to deduce the adsorption capacities of a support. The determination of the kinetic parameters must also be carried out to predict the shape of the curves. The transfer of an adsorbate from the liquid phase to an adsorption site involves the following steps [29]:

1st step: transfer of the adsorbate from the liquid phase to the boundary layer of the liquid film linked to the solid particle (by convection or diffusion). Very quick step.
2nd step: Transfer of the adsorbate through the liquid film to the external surface of the adsorbent. Quick step.
3rd step: Diffusion inside the adsorbent particle along two paths, under the influence of the concentration gradient. Slow step.
3a: In the adsorbed state, by surface diffusion. 3b: In the free state, by pore diffusion.
4th step: adsorption in a micropore. Very quick step.

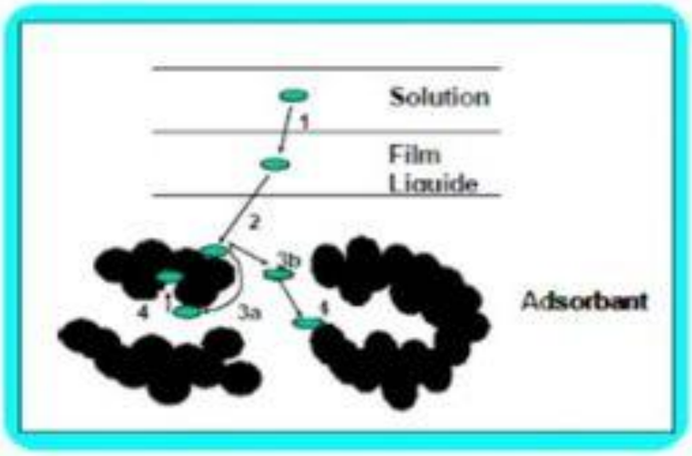

Figure I.20: The stages of adsorption kinetics

Chapter II:

Materials and Methods

II.1 Introduction

This chapter presents the methods followed and the materials used, as well as the description of the adsorption tests of basic fuchsine dye depending on the operating parameters, including the mass of the adsorbent, *p*H of solution, contact time, initial concentration, and temperature.

This work was carried out at the Process Engineering Research Laboratory at the University of Laghouat.

II.2 Apparatus and Reagents

II.2.1 Apparatus

- Magnetic stirrer (AGIMATIC-N).
- Electric sieve (SAYONA)
- Oven (MEMMERT)
- Precision analytical balance (SCALTEC)
- Stirred bath (ST 30).
- pH meter
- UV-visible spectrophotometer (SECOMEM).
- Variable volume micropipette 100-1000 µL (ORAGON LAB)
- Beakers with capacities of 100, 150, and 250 mL.
- Bottles with a capacity of 120 mL.
- Magnetic stir bars.
- Graduated cylinders with capacities of 50 and 100 mL.
- Cuvettes.
- Volumetric flasks with capacities of 100 and 500 mL.
- Filter paper.
- Test tubes of 5 mL with stands.
- Funnel.
- Nozzle.
- Spatula.
- Watch glass.
- Distilled water spray bottle.

II.2.2 Reagents

The chemicals product used in this study are listed in Table II.1.

Table II.1: The general characteristics of chemicals product used

Designation	**Sodium hydroxide**	**Sulfuric acid**	**Methylen blue**
Chemical Formula	NaOH	H_2SO_4	$C_{16}H_{18}ClN_3S$
Molecular Weight	39.997 g/mol	98.08 g/mol	319.85 g/mol
Purity	98 %	95 %	--
Mark or Brand	Biochem	Sigma-Aldrich	Biochem
Physical states			

II.2.3 Preparation of Reagents

a. Preparation of NaOH (0.1 M)

To prepare the solution, 0.4 g of NaOH (M=39.99 g/mol, Purity = 98%) is weighed. This quantity is dissolved in distilled water in a 100 mL volumetric flask, and distilled water is added until the mark.

This solution is used to adjust the *p*H.

b. Preparation of H_2SO_4 (0.1 M)

To prepare this solution, 0.30 mL of H_2SO_4 (M=98.08 g/mol, Purity = 95%, Density = 1.84 g/mL) is taken. This quantity is dissolved in distilled water in a 100 mL volumetric flask, and distilled water is added until the mark.

This solution is also used to adjust the *p*H of dye solutions.

c. Preparation of the stock solution of MB

We weigh 1g of Methylen blue using an analytical balance. This quantity is dissolved in distilled water in a 1000 mL flask, adding distilled water until the mark. The solution is stirred using a stirrer for 1 hour to obtain a homogeneous solution.

Figure II.1: The stock solution of the MB adsorbate

II.2.4 Preparation of the adsorbent

In the context of this master's thesis, the chosen adsorbent is Woodworking powder designated as WP.

The protocol for preparing the adsorbent is presented in the diagram of Figure II.2, which consists of the following 5 steps [30]: Washing, Filtration, Drying, Grinding, and Sieving.

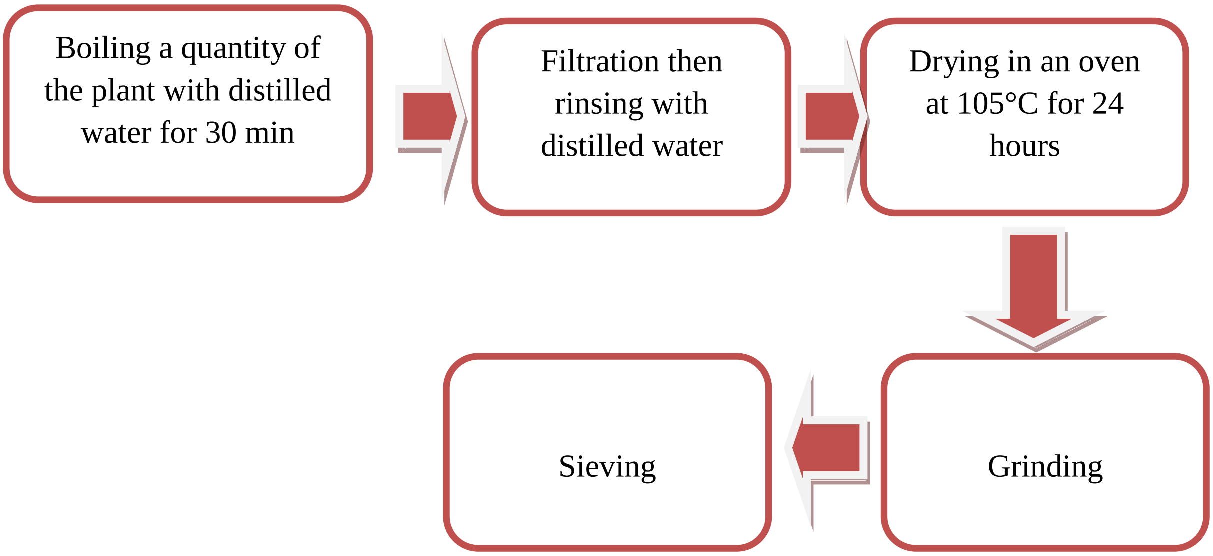

Figure II.2: Flowchart of WP adsorbent preparation.

Following these pre-treatment steps, the adsorbent is collected in powdered form as shown in Figure II.3.

Figure II.3: The WP adsorbent after preparation.

II.3 Analysis Technique (UV-Visible Spectroscopy)

The Methylen blue solution was quantified using a UV-Visible spectrophotometer (see Appendix 2). UV-Visible spectroscopy is an absorption-based analytical technique in the UV-Visible range (400-800 nm), where the absorbance of the solution is measured at the maximum wavelength (λ max = 543 nm).

The measured absorbance is related to the concentration of the solution according to the Beer-Lambert law (Equation II.1), which indicates a proportionality between these two parameters [31]:

$$A = \log (I_0/I) = \varepsilon\, L\, C \qquad \textbf{(II.1)}$$

With:

A: Absorbance of the solution

I_0: Intensity of light transmitted through the pure solvent

I: Intensity of light of that wavelength transmitted through a solution of concentration C (in mol/L) in the spectrophotometer

ε: Molar extinction coefficient (L/mol.cm)

L: Optical path length

C: Concentration of the MB solution

Figure II.4: UV-Visible Spectrophotometry**.**

II.4. Adsorption Experiments

The adsorption experiments were conducted in a batch system. A series of 120 mL capacity flasks were used to perform these various tests.

II.4.1 Effect of adsorbent mass

Different masses of the adsorbent (0.05, 0.1, 0.2, 0.5, 1g, and 1.5g) were added to 6 flasks containing 50 mL of BM solution. These flasks were agitated for 1.5 hours in a series of agitation wells.

The samples were then filtered and analyzed by UV-Visible spectroscopy

II.4.2 Effect of *p*H of solution

To determine the optimal pH for MB adsorption by WP, 0.3 g of the adsorbent was added to each of the 7 flasks. Then, 50 mL of MB solution (100 mg/L) was added to each flask, and the pH of these mixtures was adjusted to pH = 2, 4, 5, 6, 7, 8, and 10, respectively, using NaOH and H_2SO_4 reagents [28].

The mixtures were agitated for 1.5 hours, and then the samples were filtered. The absorbance was measured using a UV-Visible spectrophotometer.

II.4.3 Effect of Contact Time

Eight flasks were prepared, and in each flask, 0.2 g of WP adsorbent was mixed with 100 mL of MB solution. The 8 flasks were agitated for 3, 5, 10, 15, 30, 60, 90, 120, and 180 minutes, respectively.

After the contact time elapsed, the agitation was stopped, and each sample was filtered separately. The absorbance was then measured using a UV-Visible spectrophotometer. The same experimental procedure was carried out for each MB adsorbate solution at concentrations of 25, 50, 75, 100, and 200 ppm or mg/L.

II.4.4 Effect of Initial Concentration

To study the effect of concentration, the following steps were followed:

Five flasks were prepared with different initial concentrations of 25, 50, 75, 100, and 200 ppm. Each flask was then mixed with 0.4 g of the adsorbent, and the mixture was subjected to agitation for 30 minutes.

II.4.5 Effect of Temperature

To determine the effect of temperature on pollutant adsorption, 0.3 g of WP adsorbent was weighed and 50 mL of MB solution was added.

Using a temperature-controlled agitation bath, the solution temperature was maintained at 25, 35, and 45°C for 30 minutes at a speed of 150 rpm.

Chapter II:

Results and Discussion

III.1. Introduction

In this final chapter, we move on to studying and evaluating the efficiency of powder in woodworking in removing methylene blue and the factors affecting this, such as the pH of the solution, the dose of adsorbent and the concentration of methylene blue. And study kinetic and isothermal modeling to determine the most appropriate models to describe the adsorption process

III.2. Effect of physic-chemical factors

III.2.1. Effect of mass adsorbent

The effect of adsorbent mass on adsorption plays a significant role in determining the efficiency and effectiveness of adsorption processes, impacting pollutant removal rates and overall system performance [30].

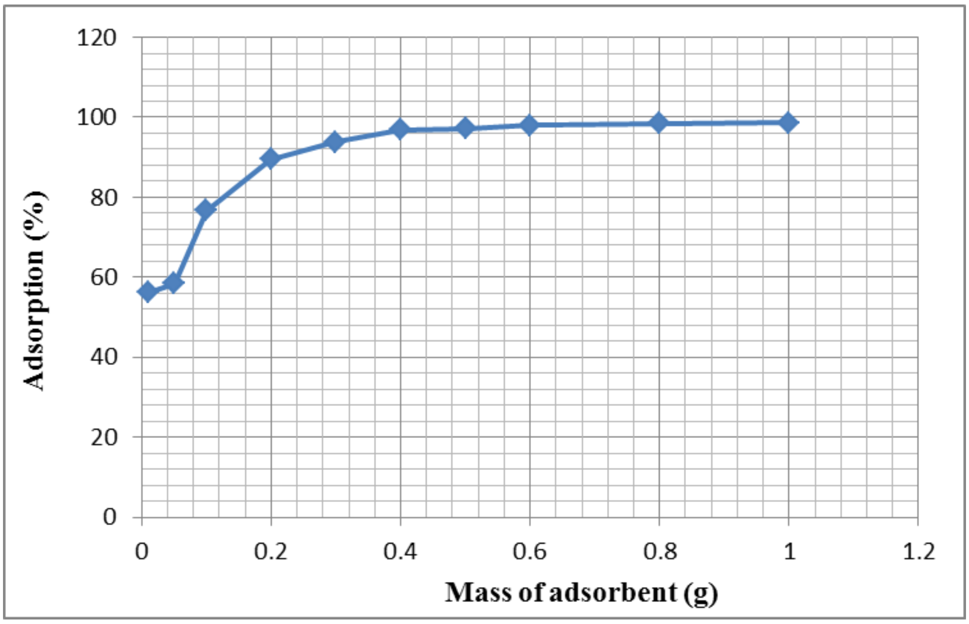

Figure III.1: Effect of mass adsorbent on MB adsorption onto the WP adsorbent (Conditions: initial concentration 100 mg/L, time 90 min, temperature 25°C, agitation speed 150 rpm).

The curve in Figure III.1 shows that the percentage of MB elimination is practically 98% by Woodworking pawder. And the Woodworking pawder mass which will be taken into account in subsequent studies will be 0.4 g.

III.2.2. Effect of *p*H

Effect of pH is an important factor in any adsorption study, as it can influence the adsorbent and adsorbate structure as well as the adsorption mechanism [31].

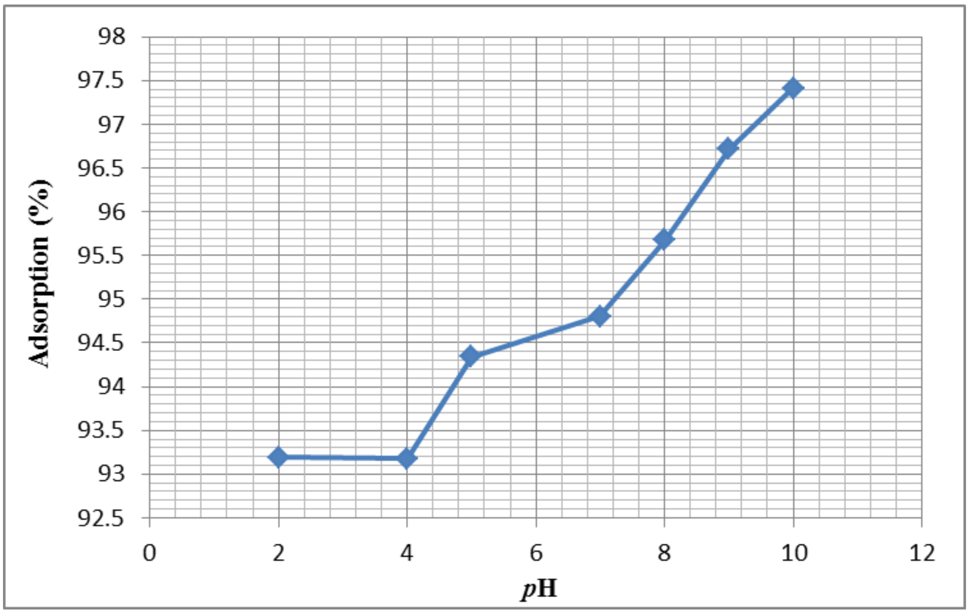

Figure III.2: Effect of pH on MB adsorption onto the WP adsorbents (Conditions: initial concentration 100 mg/L, time 90 min, temperature 25°C, agitation speed 150 rpm) .

The effect of pH change on the adsorbed quantity was studied by changing the pH from 2 to 10 of the data and graphs obtained (Figure III.2). We observe a significant increase in the adsorption yield in the pH range studied up to the pH value equal to 10. We therefore conclude that the availability of sites for ionic dye repair is based on pH.

III.2.3. Effect of contact time

The contact time that occurs between the biosorbent and the adsorbent greatly affects the efficiency of the of the biosorption process. Contact time is the time required for the biosorbent to be able to interact with the adsorbent optimally at a given time in order to optimally bind the adsorbent [32].

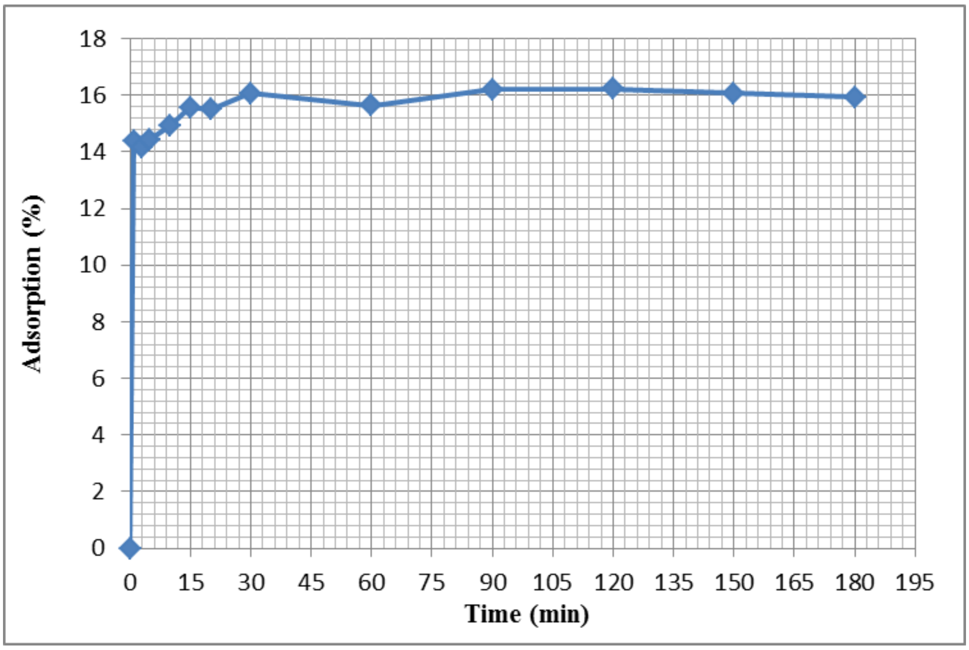

Figure III.3: Effect of contact time on MB adsorption onto the WP adsorbents (Conditions: initial concentration 100 mg/L, temperature 25°C, agitation speed 150 rpm).

Figure (III.3) shows the adsorption results obtained for blue methylene the adsorbent. We note that the elimination rate increases with time until a part saturation level or this ratio no longer changes showing that the adsorbent-adsorbate interaction has reached equilibrium.

The adsorption curve indicates that equilibrium is reached after 30 minutes. This means the amount of adsorbate no longer increases with further contact time. All adsorption experiments will be carried out for an adsorbate contact time of 30 minutes, a time assumed to be sufficient for this adsorption.

III.2.3. Effect of temperature and initial concentration

The effect of temperature is another important parameter of the physico chemical process, because the temperature will change the adsorption capacity of the adsorbent [33].

Moreover, the initial concentration of the adsorbate in the solution directly affects the adsorption capacity of the adsorbent.

Temperature affects the kinetics and thermodynamics of adsorption, while the initial concentration of the adsorbate impacts the adsorption capacity of the adsorbent [34].

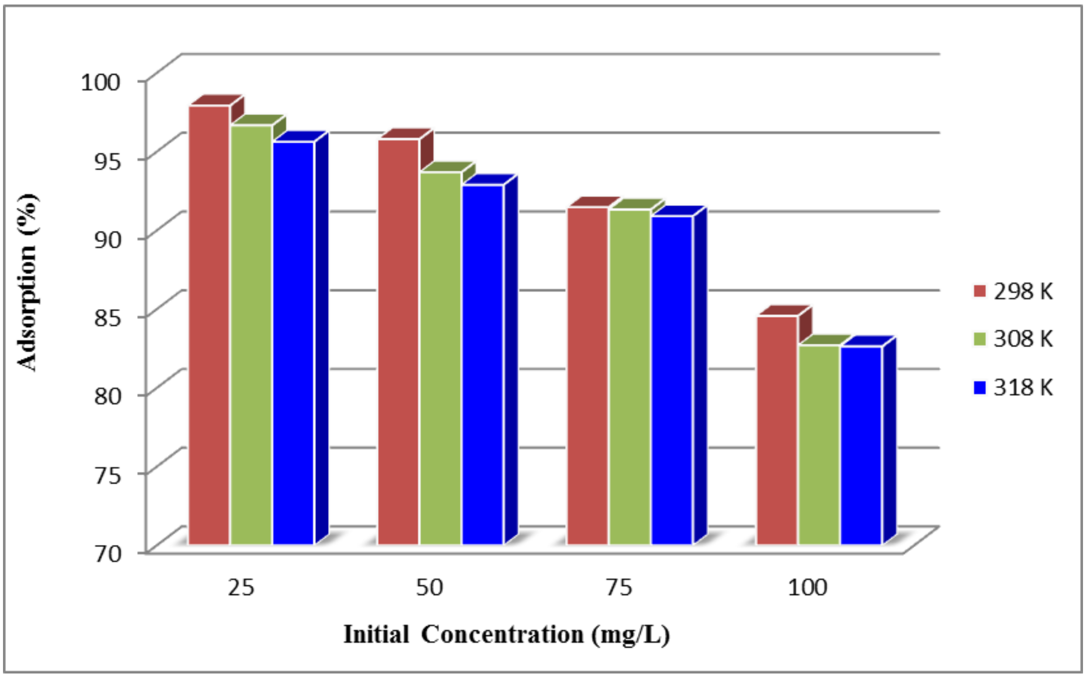

Figure III.4: Effect of temperature and initial concentration on MB adsorption onto the WP adsorbents (Conditions: time 30 min, agitation speed 150 rpm).

From figure (III.4), we see that the elimination rate of blue methylene decreases with increasing temperature.

Additionally, an increase in the initial concentration of methylene blue also results in a decrease in the elimination rate, indicating an inverse relationship between initial concentration and removal efficiency.

These trends can be attributed to the complex interplay of factors such as the impact of temperature on the adsorption process, the desorption of methylene blue molecules from the adsorbent surface, and the saturation of adsorption sites at higher initial concentrations. The decrease in elimination rate with increasing temperature and initial concentration underscores the importance of carefully controlling these parameters in adsorption studies to optimize the removal efficiency of pollutants like methylene blue.

Therefore, the results indicate that the optimum concentration is 25 mg/L and the optimum temperature is 298 K for this adsorption.

III.3. Kinetics Studies

Adsorption kinetics is a fundamental aspect of understanding the rates at which adsorption processes occur, providing enabling the quantification of adsorption rates, equilibrium times, and the mechanisms governing the adsorption process over time.

The kinetics of adsorption has been studied extensively, leading to the development of various kinetic models such as the Lagergren equation of pseudo-first-order, and pseudo-second-order models. These models help in characterizing the adsorption process, determining the rate constants, and understanding the mechanisms underlying adsorption phenomena.

The pseudo-first order model (PFO) [35]:

The expression is given by Lagergren: Linearizing the previous equation gives (1):

$$\text{Ln}\ (q_e\text{-}q_t) = \ln q_e - k_1\ t\text{.........}(1)$$

We trace In $(q_e\text{-}q_t) = f\ (t)$, we obtain a line which gives k_1, and q_e

k_1: first order rate constant for adsorption of MB on WP in (g/mg/min).

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

q_t: quantity adsorbed at time ten (mg/g).

t: contact time in (min).

This model makes it possible to describe the phenomena taking place during the first minutes of the adsorption process [36].

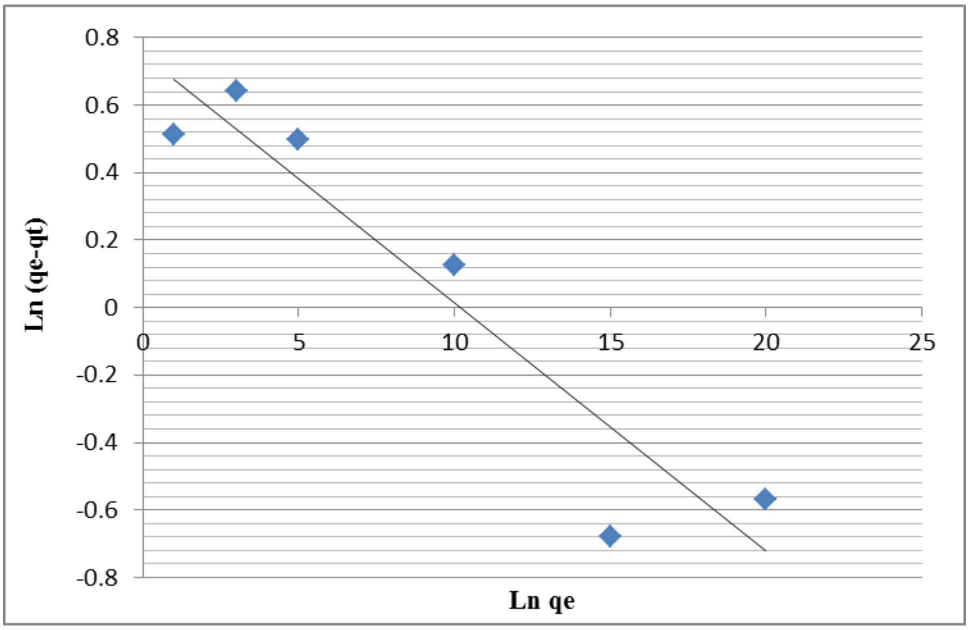

Figure III.5: Pseudo-first-order kinetic fit for MB adsorption onto WP

The pseudo-second order (PSO) model [37]:

The pseudo-second-order (PSO) model is given by the following expression (2):

$$1/q_t=1/(k_2.q_e^2) + (1/q_e)\ t\text{..........}(2)$$

k_2: second order reaction rate constant for adsorption of MB on WP in (g/mg/min).

qe: quantity adsorbed at equilibrium in (mg/g).

q_t: quantity adsorbed at time ten (mg/g).

t: contact time in (min).

We trace $t/q_t = f(t)$, we obtain a line which gives k_2, and q_e

Unlike the first-order model, the pseudo-second-order model is applicable to a wider time interval (usually the entire adsorption process).

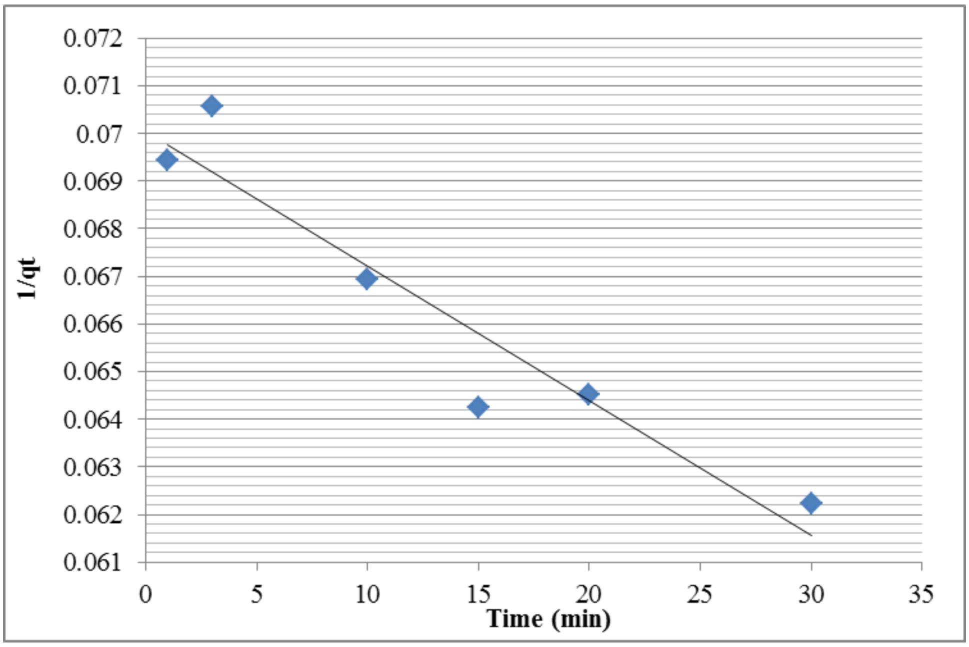

Figure III.6: Pseudo-second-order kinetic fit for MB adsorption onto WP

Through the curves (Figures III.5-III.6), the kinetic parameters for each model were calculated and the results are shown in the table III.1

Table III.1: Kinetics models parameters for the adsorption of MB dye onto WP.

Kinetic model	**Parametres**	**BM** **(C=100 mg/L)**
Pseudo-first-order	k_1 (1/min) qe exp (mg/g) qe cal (mg/g) R^2	0.0735 16.069 2.116 0.8844
Pseudo-second order	k_2 (g / (mg min)) qe exp (mg/g) qe cal (mg/g) R^2	0.0003 16.069 14.26 0.9063

According to the calculations of the pseudo-first order and second order kinetic parameters we note that the pseudo-first order rate constant (k_1) is much higher than that of the second order (k_2). As well as the experimental equilibrium adsorption capacity q_e(exp) of the first order equal to the equilibrium adsorption capacity q_e(exp) of the kinetics of the second order, In the other side for kinetics of the pseudo- second order the value of the calculated equilibrium adsorption capacity q_e(cal) of second order greater than the value of the calculated equilibrium adsorption capacity q_e(cal) of pseudo-first order.

It is also noted that the kinetics of elimination of methylene blue agrees better with the pseudo-second order model with an excellent correlation coefficient (R^2=0.9063), which is greater than the correlation coefficient of the pseudo- first order model.

III.4. Isotherm Studies

The study of adsorption isotherms allows us to better understand how the adsorbed MB molecules interact with the adsorbent (WP). Adsorption isotherms provide many fundamental physicochemical data to estimate the applicability of the adsorption process express the surface properties and affinity of the adsorbent and can also be used to find the maximum adsorption capacity of an adsorbent [38].

The Langmuir Isotherm model predicts the formation of a single layer of the adsorbed molecules (molecular monolayer) on specific sites, and without interaction between them with a heat of adsorption independent of the surfac [39].

Langmuir Isotherm model is given by the following expression (3):

$$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{k_{l*q_m}}\,\frac{1}{c_e} \qquad (3)$$

with:

q_e: Quantity of substance adsorbed at equilibrium (mg/g).

q_m: Adsorption capacity at saturation (mg/g).

C_e: Equilibrium substrate adsorbate concentration (mg/L).

K_L: Langmuir constant .

We trace 1/q_e as a function of 1/C_e we obtain a line which gives, the constant q_m and K_L are respectively the slope and ordinate at the origine of the line.

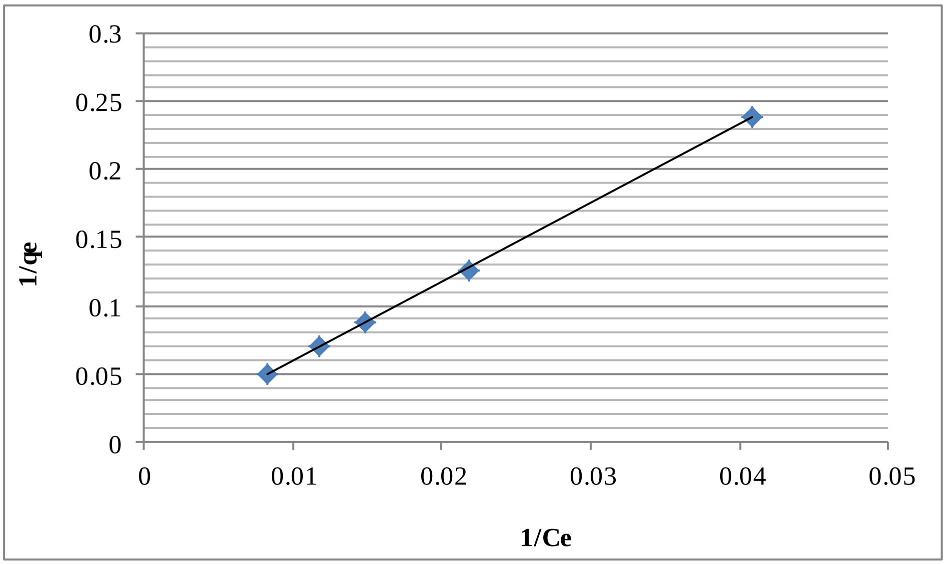

Figure III.7: Langmuir isotherm fit for MB adsorption onto WP.

The Freundlich isotherm model assumes heterogeneity of the adsorption surface with sites of different adsorption energy, as well as the possibility of formation of multilayers of the adsorbed molecules in equilibrium with each other [40].

Freundlich isotherm model is given by the following expression (4):

$$\text{Ln } q_e = \ln K_f \text{ x } \frac{1}{n} \ln C_e \qquad (4)$$

With:

Ce: Adsorbate concentration at adsorption equilibrium (mg/L)

qe: Quantity adsorbed

K_F: Freundlich constants

We trace ln qe as a function of ln Ce we obtain a line which gives, slope 1/n and ordinate at origin Ln $K_{F.}$

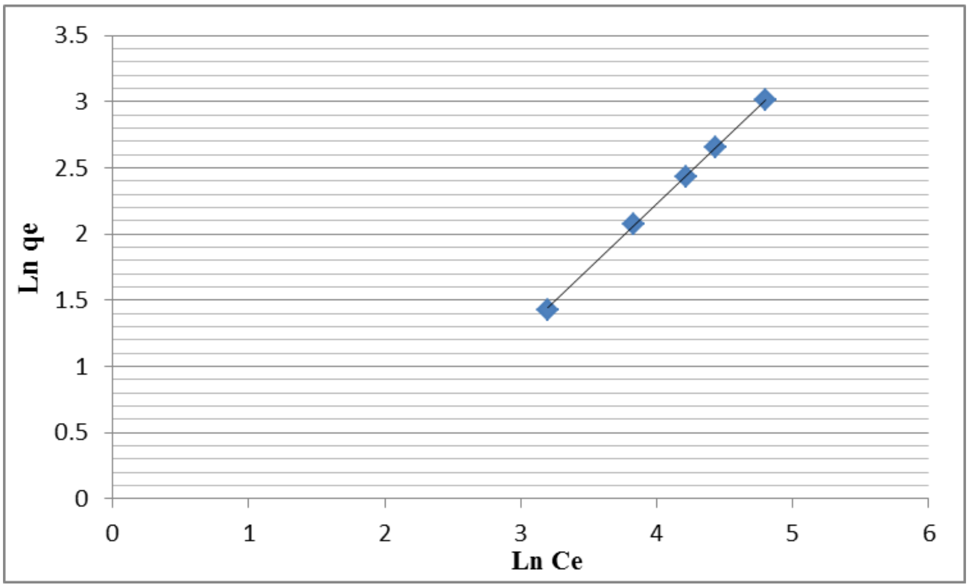

Figure III.8: Freundlich isotherm fit for MB adsorption onto WP.

Through the curves (Figures III.7-III.8), the kinetic parameters for each model were calculated and the results are shown in the table III.2

Table III.2: Isotherms models parameters for the adsorption of MB dye onto WP

Isotherm model	**Parametres**	**BM** **(T=298 K)**
Langmuir	K_L (1/min) q_m(mg/g) qe cal (mg/g) R^2	0.0018 90.909 16.069 0.9997
Freundlich	K_f (g/(mg min)) 1/n (mg/g) R^2	0.1835 0.9807 0.9996

These results show that the parameters of the isotherms and the correlation coefficients R^2 of two models Langmuir and Freundlich for the linear form, are very high but the correlation coefficients of Langmuir is greater than the correlation coefficient of the model Freundlich, Therefore the dye adsorption isotherm is well described by the Langmuir isotherm with the the maximum adsorption capacity about 90.90 mg/g.

III.5.Comparative study

In the following table III.3, some results of previous studies on the adsorption of methylene blue have been collected to make a comparison with the results we obtained in this study.

Table III.3: Adsorption of methylene blue on different adsorbents.

Adsorbent	**q_m (mg/g)**	**Isotherm model**	**References**
P. brutia cones	109.76	Langmuir	[41]
Activated charbon	86.20	Langmuir	[42]
Date pits	16.10	Langmuir	[43]
Pea pods	45.45	Langmuir	[44]
Woodworking pawder	90.90	Langmuir	This study

By comparing the results obtained in our study with those of previous research, we can conclude that the adsorbent utilized demonstrated a satisfactory and competitive adsorption capacity for methylene blue.

General Conclusion

This study aimed to optimize a process for treating water contaminated by dyes. The selected process is adsorption on woodworking powder prepared locally in the laboratory. The results demonstrated effective elimination of the chosen organic pollutant.

The investigation focused on several parameters influencing the fixation of the dye, including pH, mass of the adsorbent, contact time, and temperature, with the objective of optimizing the adsorption of blue methylene on the prepared woodworking powder.

The study of the effect of pH revealed a maximum fixation efficiency of 97.5% at pH=10. The retention of methylene blue by the woodworking powder occurs rapidly during the initial minutes of contact until equilibrium is reached after approximately 30 minutes, beyond which no further adsorption occurs. Adsorption of methylene blue increases with the amount of adsorbent introduced, with the optimal adsorbent mass estimated at 0.4 g. Furthermore, adsorption decreases with increasing initial concentration of methylene blue and temperature.

Kinetic modeling indicated that the pseudo-second order model best describes the kinetics of adsorption of methylene blue onto woodworking powder.

This adsorption process was evaluated using common isotherm models such as Langmuir and Freundlich. Among these, the Langmuir isotherm model best describes the adsorption tests, with an adsorption capacity of 90.90 mg/g.

A comparison study with some adsorbents proved that the adsorbent used in this study achieved a sufficient and very good result, in addition to the fact that this adsorbent is environmentally friendly and inexpensive, which makes it a good alternative to traditional adsorbents.

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عنوان المذكرة: تثمين مادة طبيعية لإزالة ملوث صناعي

اللقب: سعداوي **الإسم:** اسماء **المؤطر:** د. بوداود اسماء
اللقب: حمري **الإسم:**هجيرة

ملخص: الهدف من هذا العمل هو دراسة إمكانية امتزاز صبغة الميثيلين الازرق بواسطة مساحيق النجارة، وتزداد كفاءة الامتزاز لمسحوق النجارة مع زيادة كتلة المادة الماصة ودرجة الحموضة، وتتناقص مع زيادة تركيز أزرق الميثيل الأولي ودرجة الحرارة. أظهرت التجارب الحركية أن الامتزاز سريع ومطابق لنموذج الترتيب الثاني الزائف، بينما أظهرت التجارب المتساوية الحرارة أن نموذج لونجمير هو الأكثر ملائمة لهذا الامتزاز، حيث بلغت كفاءة الامتزاز 90,90 ملغم/غم تحت ظروف التشغيل المثلى.

كلمات مفتاحية: مسحوق النجارة ، الميثيلين الازرق ، الامتزاز ، المياه العادمة ، الحركية ، والمتساوي الحرارية.

Memory title: Valorization of natural material for the removal of an industrial pollutant

Name: SAOUDI **First name: ASMAA** **Directed by: Dr BOUDAOUD Asma**
Name: HAMRI **First name: HADJIRA**

Abstract: The aim of this work is to study the possibility of adsorption of methylene blue dye by woodworking powder, The adsorption efficiency of woodworking powder increases with increasing sorbent mass and pH, and decreases with increasing initial methyl blue concentration and temperature. Kinetic experiments showed that the adsorption is fast and conforms to the pseudo-second order model, while isothermal experiments showed that the Langmuir model is the most appropriate for this adsorption, with adsorption efficiency equal to 90, 90 mg/g under optimum operating conditions.

Key words: Woodworking powder, Methylene blue, Adsorption, Wastewater, Kinetics, and Isotherm.

Titre du mémoire : Valorisation de matériau naturel pour l'élimination d'un polluant industriel.

Nom : SAOUDI **Prénom : ASMAA** **Encadreur : Dr BOUDAOUD Asma**
Nom : HAMRI **Prénom : HADJIRA**

Résumé: Le but de ce travail est d'étudier la possibilité d'adsorption du colorant bleu de méthylène par la poudre à bois. L'efficacité d'adsorption de la poudre à bois augmente avec l'augmentation de la masse absorbante et du pH, et diminue avec l'augmentation de la concentration et de la température initiales du bleu de méthyle. Les expériences cinétiques ont montré que l'adsorption est rapide et conforme au modèle pseudo-seconde ordre, tandis que les expériences isothermes ont montré que le modèle de Langmuir est le plus approprié pour cette adsorption, avec une efficacité d'adsorption égale à 90,90 mg/g dans des conditions opératoires optimales.

Mots clés : Poudre à bois, Bleu de méthylène, Adsorption, Eaux usés, Cinétique, et Isotherme.