



Université Mohamed Kheider de Biskra  
Faculté Des Sciences Exactes Et Des Science De La Nature et de la Vie  
Département Des Science De La Nature

# MÉMOIRE DE MASTER

Domaine : Sciences de la Matière

Filière : Chimie

Spécialité : Chimie des matériaux

Réf. : CH01

---

Présenté et soutenu par :

**Hafsa CHATTEH**

Le : 27/05/2024

## Development of adsorption capacity on activated carbon prepared from ziziphus by chemical activation

---

### Jury :

Dr	Kamel DJAIL	MCA	Université Med Khider Biskra	Président
Dr	Elies OMARI	MCB	Université Med Khider Biskra	Examineur
Dr	Amira OUAKKAF	MCA	Université Med Khider Biskra	Promotrice

Année universitaire : 2023-2024

## ***Acknowledgements***

*First of all, I would like to thank Allah, the Almighty, for giving me the strength, courage, patience and willpower to complete this modest work.*

*All this work took place at the Chemistry Laboratory of the Department of Matter Sciences at the University Mohamed Khaider-Biskra.*

*I would particularly like to thank **Dr.Amira OUKKAF**, Senior Lecturer, who supervised me and provided me with guidance throughout the writing of this dissertation.*

*I would like to express my gratitude to her for passing on to me her sense of pedagogy and her attention to detail.*

*I would also like to express my respectful thanks to the members of the jury **Dr.Kmel DJAIL** and **Dr.Elies OMARI**, for having done me the honor of chairing the Jury and for their kind participation.*

*Many thanks to all the Chemistry Laboratory Engineers in our Department, I also owe a debt of gratitude to all the chemistry teachers who followed me throughout my studies.*

*Last but not least, my warmest thanks go to my friends and colleagues who have always helped and encouraged me.*

*Thank you very much.*

*CHETTAH Hafsa*

# *Dedication*

*I dedicate this modest work to*

*To myself that didn't give up*

*To my dear parents,*

*Your unwavering love, support, sacrifice and encouragement have been the main motivation for me to move forward.*

*This thesis is a testament to your endless dedication and the values you instilled in me. Thank you for being my guiding light.*

*To my beloved sisters;*

*Your love, compassion and unwavering faith in me has been a driving force. Your encouragement and wise words have filled my path with light. Thank you for being my source of strength.*

*To my dear friends;*

*You have accompanied me throughout my academic career and have been a great companion and support, Thank you Ikhlas, Amani, Fadwa, Hadjir, Rania.*

*CHETTAH Hafsa*

# Table of contents

---

## ***TABLE OF CONTENTS***

**ACKNOWLEDGEMENTS**

**DEDICATION**

**ABSTRACT**

**LISTE OF FIGURES**

**LISTE OF TABLES**

**ACRONYMS**

### **GENERALE INTRODUCTION**

	1
Bibliographic References.....	3

### **CHAPTER I**

#### **BIBLIOGRAPHIC RESEARCH**

I.1. Introduction.....	4
I.2. Water pollution.....	4
I.2.1. Sources of water pollution.....	5
I.3. Dyes.....	6
I.3.1. Definition.....	6
I.3.2. Classification of dyes.....	6
I.3.3. Congo red.....	7
I.4. Adsorption.....	8
I.4.1. Definition.....	8
I.4.2. Types of adsorption.....	9
I.4.3. Adsorption kinetic models.....	9
I.4.4. Isotherm adsorption.....	10
I.4.4.1. Classification of adsorption isotherms.....	10
I.5. Activated carbons.....	12
I.5.1. Methods for producing activated carbon.....	12
I.5.2. Types of Activated Carbon.....	12
I.5.3. Applications of Activated Carbon.....	14
I.6. Characterization techniques.....	15
I.6.1. Fourier transform infrared spectroscopy (FTIR).....	15
I.6.2. Scanning electron microscopy (SEM).....	13
I.6.3. Brunauer isotherm- Emette- Teller (BET).....	13
I.6.3.1. Principle, measurand and measurement.....	13

## Table of contents

---

I.6.4. UV-Vis Spectrophotometry.....	17
I.7. Conclusion.....	18
Bibliographic References.....	19
<b><u>CHAPTER II</u></b>	
<b><u>METHODS, RESULTS AND DISCUSSIONS</u></b>	
II.1. Introduction.....	23
II.2. The raw material (ziziphus Lotus seeds).....	23
II.3. Synthesis of activated carbons.....	24
II.3.1. Preparation of activated carbon (AC1).....	25
II.3.1.1. Results and discussion.....	30
II.3.1.1.1. Fourier transform infrared spectroscopy (FTIR).....	30
II.3.1.1.2. Scanning electron microscopy Surface morphology (SEM)...	32
II.3.1.1.3. Textural characterization.....	33
II.3.1.1.4. CR adsorption on the synthesized (AC1) under optimized conditions.....	35
II.3.2. Preparation of activated carbon (AC2).....	37
II.3.2.1. Results and discussion.....	39
II.3.2.1.1. Fourier transforms infrared spectroscopy (FTIR).....	39
II.3.2.1.2. Scanning electron microscopy (SEM).....	40
II.3.2.1.3. Textural characterization of (AC2).....	40
II.3.2.1.4. CR adsorption on the synthesized AC2 under optimized conditions.....	41
II.4. Conclusion.....	42
Bibliographic References.....	43
<b>GENERAL CONCLUSION</b> .....	45

## Abstract

Activated carbons were prepared from Ziziphus Lotus seeds using chemical activation by NaOH. They were then used to remove a reactive congo red dye. Carbons AC1 and AC2 obtained by two different preparation methods were characterised by N<sub>2</sub> adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The BET surface area of AC1 and AC2 was 37.6432 and 9.7211 m<sup>2</sup>/g respectively. The effects of the initial dye concentration CR, contact time and activated carbon mass were study Finally, the results indicate that AC1 carbon can be considered a low-cost material for the removal of CR dye and dyes from dye wastewater.

**Keywords:** Activated carbon, ziziphus, adsorption optimisation, Matlab, congo red.

## Résumé

Charbons actifs ont été préparés à partir de noyau de Ziziphus Lotus en utilisant l'activation chimique par NaOH. Ils ont ensuite été utilisés pour éliminer un colorant réactif rouge congo. Les charbons AC1 et AC2 obtenus par deux méthodes de préparation différentes ont été caractérisés par des isothermes d'adsorption-désorption de N<sub>2</sub>, la spectroscopie infrarouge à transformée de Fourier (FTIR), la microscopie électronique à balayage (SEM). La surface apparente BET du AC1 et du AC2 était respectivement de 37.6432 et 9.7211 m<sup>2</sup>/g. L'optimisation de l'adsorption du rouge congo a été étudiée par les effets de la concentration initiale de colorant, du temps de contact, et de la masse du charbon actif. Enfin, les résultats indiquent que le charbon AC1 peut être considéré comme un matériau peu coûteux pour l'élimination du colorant CR et des colorants dans les eaux usées des colorants.

**Mots-clés :** Charbon actif, ziziphus, optimisation de l'adsorption, Matlab, Rouge Congo.

## ملخص

تم تحضير الكربونات المنشطة من لب زيزيفوس لوتس عن طريق التنشيط الكيميائي باستخدام هيدروكسيد الصوديوم، التي تم استعمالها بعد ذلك لإزالة صبغة تفاعلية هي الكونغو الأحمر. تم توصيف الكربونات AC1 و AC2 المتحصل عليها بطريقتين مختلفتين للتحضير عن طريق متساوي الامتزاز والامتصاص N<sub>2</sub> ومتساوي الامتصاص، والتحليل الطيفي بالأشعة تحت الحمراء المحولة لفورييه (FTIR)، والفحص المجهر الإلكتروني الماسح (SEM). كانت مساحة سطح (BET) ل AC1 و AC2 37.6432 و 9.7211 م<sup>2</sup>/غ على التوالي. تمت دراسة تحسين امتزاز الكربون المنشط لصبغة الكونغو الأحمر باستخدام تأثيرات تركيز الصبغة الأولية، ووقت التلامس وكتلة الكربون المنشط. أخيرًا، تشير النتائج إلى أن كربون AC1 يمكن اعتباره مادة منخفضة التكلفة لإزالة صبغة CR والأصبغ من مياه الصرف الصحي الصبغية.

**الكلمات المفتاحية:** الكربون المنشط، زيزيفوس، تحسين الامتزاز، ماتلاب، الكونغو الأحمر.

## List of figures

# List of figures

### Chapter I: Bibliographic research

<b>N°</b>	<b>Figure</b>	<b>Page</b>
<b>I.1</b>	<i>Dyes classification</i> .....	6
<b>I.2</b>	<i>Molecular structure of CR</i> .....	7
<b>I.3</b>	<i>The adsorption phenomenon inside an adsorbent grain</i> .....	8
<b>I.4</b>	<i>Different types of gas adsorption isotherms according to I.U.P.A.C.</i> .....	11
<b>I.5</b>	<i>Powdered Activated Carbon (PAC)</i> .....	13
<b>I.6</b>	<i>Granular Activated Carbon (GAC)</i> .....	13
<b>I.7</b>	<i>Extruded Activated Carbon</i> .....	13
<b>I.8</b>	<i>Activated Carbon Fiber (ACF)</i> .....	14

### Chapter II: Methods, Results and discussions

<b>II.1</b>	<i>Ziziphus Lotus tree and its fruits</i> .....	24
<b>II.2</b>	<i>Activated carbon(AC1) preparation protocol</i> .....	25
<b>II.3</b>	<i>Washed Ziziphus seeds</i> .....	26
<b>II.4</b>	<i>Oven-dried seeds</i> .....	26
<b>II.5</b>	<i>Grinders and the grinded seeds</i> .....	27
<b>II.6</b>	<i>Sieving machine</i> .....	27
<b>II.7</b>	<i>Calcining the pellets product in the oven</i> .....	28
<b>II.8</b>	<i>Impregnated granules</i> .....	29
<b>II.9</b>	<i>Calcining the pellets product in the oven (Second time)</i> .....	29
<b>II.10</b>	<i>.Activated carbon washed with HCl and water With PH measurement</i> .....	30
<b>II.11</b>	<i>Pellet preparation</i> .....	31
<b>II.12</b>	<i>Fourier transform infrared spectrometer FTIR- Shimadzu FTIR-840</i> .....	31
<b>II.13</b>	<i>Infrared spectrum of activated carbon(AC1)</i> .....	31
<b>II.14</b>	<i>SEM photograph of The raw material (RM) and activated carbon (AC1)</i> .....	33
<b>II.15</b>	<i>The Nitrogen adsorption-desorption isotherms at -196,011 °C of AC1</i> .....	34
<b>II.16</b>	<i>The experimental setup used for CR adsorption on the synthesized AC1 under optimized conditions</i> .....	35
<b>II.17</b>	<i>UV-Visible spectrophotometry PerkinElmer UV/VIS Spectrometer Lambda</i> ...	36
<b>II.18</b>	<i>Activated carbon (AC2) preparation protocol</i> .....	38
<b>II.19</b>	<i>Infrared spectrum of activated carbon (AC2)</i> .....	39
<b>II.20</b>	<i>SEM images of Activated Carbons (AC1) and (AC2)</i> .....	40

## List of figures

---

<b>II.21</b>	<i>The Nitrogen adsorption-desorption isotherms at -196,011 °C of AC2.....</i>	41
--------------	--	----



## Acronyms

---

# Acronyms

<b>AC1</b>	Activated Carbon 1
<b>AC2</b>	Activated Carbon 2
<b>CR</b>	Congo Red
<b>FTIR</b>	Fourier transform infrared spectroscopy
<b>SEM</b>	Scanning electron microscopy
<b>BET</b>	Brunauer-Emmett-Teller
<b>NaOH</b>	sodium hydroxide
<b>HCl</b>	hydrochloric acid

## List of tables

---

# List of tables

### ***Chapter I: Bibliographic research***

<b><i>N°</i></b>	<b><i>Tables</i></b>	<b><i>Page</i></b>
<b><i>I.1</i></b>	<i>Characteristics of point and nonpoint sources of chemical inputs to receiving waters.....</i>	<i>5</i>
<b><i>I.2</i></b>	<i>Main chromophore and auxochrome groups, classified by intensity.....</i>	<i>6</i>
<b><i>I.3</i></b>	<i>Toxic effects showed by CR and the affected targets.....</i>	<i>8</i>
<b><i>I.4</i></b>	<i>General characteristics of physisorption and chemisorption.....</i>	<i>9</i>
<b><i>I.5</i></b>	<i>Adsorption kinetic models.....</i>	<i>10</i>

### ***Chapter II: Methods, Results and discussions***

<b><i>II.1</i></b>	<i>Matrix of main effects (ACI).....</i>	<i>37</i>
--------------------	--	-----------

*General  
Introduction*

### **General Introduction**

The rapid growth of cities and the spread of factories across different areas present a significant challenge to humanity in the 21st century through water pollution. Treating pollutants in water often proves challenging due to the wide range of pollutants with different structures [1].

Hence, it's crucial to treat this wastewater. A range of analytical techniques has been employed for removing these harmful substances from wastewater, including electrochemical oxidation, sensors, microbial breakdown, chemical coagulation, and filtration membranes [2].

In wastewater treatment, the adsorption method stands out for its simplicity in design, wide availability of adsorbents, and cost-effectiveness. Notably, activated carbon derived from agricultural by-products, processed through chemical and physical activation techniques, emerges as a promising alternative adsorbent. This method capitalizes on the abundance of agricultural waste and offers a straightforward yet efficient approach to removing pollutants from wastewater, making it an attractive option for addressing water pollution challenges [3]. there has been a growing trend of using agricultural waste such as white sapote seeds, grape stalks, orange peels, melon seeds, and sewage sludge and others [4,5,6].

Activated carbon is used in different applications due to its high porosity and large surface area. It is commonly utilized in water and air purification to remove contaminants like dyes and odors [7].

Congo red is a synthetic azo dye is used to study dye pollution in aqueous environments. However, it poses several dangers: it is toxic if ingested or inhaled, can cause skin and eye irritation, is potentially carcinogenic, and is harmful to aquatic life, contributing to environmental pollution [8].

The overall objective is to study the performance of activated carbons prepared from local biomass (*Ziziphus Lotus*) for the adsorption of Congo red in aqueous solution. The retention process of this molecule was modeled and optimized using experimental design methodology.

## ***General Introduction***

---

To thoroughly understand the mechanisms of adsorption on activated carbon and the phenomena involved, we propose to follow the following timeline:

- In the first chapter, an in-depth literature review on water pollution, adsorption phenomena, pollutants, dyes...etc.
- In the second chapter, a study was carried out on the use and development of one of our country's natural products (*Ziziphus lotus*) for the production of two activated carbons by chemical activation with NaOH using two different methods, along with physico-chemical characterization using nitrogen adsorption-desorption isotherms (BET), SEM, EDX, and FTIR. Additionally, Congo red dye was employed as a model molecule to evaluate the adsorption capacity of the synthesized activated carbons. The "experiment execution" stage involves conducting all the tests outlined in the experimental plan and subsequently collecting the test results, optimising the best adsorption condition for congo red was carried out using Matlab.

### **Bibliographic References**

- [1] Benkhaya S, M' Rabet S and El Harfi A 2020. A review on classifications, recent synthesis and applications of textile dyes Inorg. Chem. Commun. **115** 107891.
- [2] Feng P, Li J, Wang H and Xu Z 2020. Biomass-Based Activated Carbon and Activators: Preparation of Activated Carbon from Corncob by Chemical Activation with Biomass Pyrolysis Liquids ACS Omega **5** 24064–72.
- [3] Mohanty K, Das D and Biswas M N 2005. Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by ZnCl<sub>2</sub> activation Chem. Eng. J. **115** 121–31.
- [4] Arami-Niya A, Daud W M A W and Mjalli F S 2011. Comparative study of the textural characteristics of oil palm shell activated carbon produced by chemical and physical activation for methane adsorption Chem. Eng. Res. Des. **89** 657–64.
- [5] Adekola F and Adegoke H 2005. Adsorption of Blue-Dye On Activated Carbons Produced from Rice Husk, Coconut Shell and Coconut Coirpith Ife J. Sci. **7**.
- [6] Hameed B H, Ahmad A L and Latiff K N A 2007. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust Dyes Pigments **75** 143–9.
- [7] Angin D 2014. Production and characterization of activated carbon from sour cherry stones by zinc chloride Fuel **115** 804–11.
- [8] Dehghanian N, Ghaedi M, Ansari A, Ghaedi A, Vafaei A, Asif M, Agarwal S, Tyagi I and Gupta V K 2016. A random forest approach for predicting the removal of Congo red from aqueous solutions by adsorption onto tin sulfide nanoparticles loaded on activated carbon Desalination Water Treat. **57** 9272–85.

*Chapter I:*  
*Bibliographic*  
*research*

## **I.1. Introduction**

Water is one of the most important resources on the earth; it is a renewable resource vital to sustaining all forms of life, food production, textiles, cosmetics, economic development, and overall well-being. Organic dyes and antibiotic contamination pose significant threats to water ecosystems due to their toxicity and persistence. Their presence in water bodies can have adverse effects on aquatic life and human health.

Water pollution, a pressing global issue, stems from various sources including industrial effluents. Among these pollutants, dyes pose a significant threat due to their persistence and toxicity. To combat this, activated carbon emerges as a promising solution. Activated carbon, with its porous structure, exhibits remarkable adsorption capabilities, effectively removing dyes from contaminated water bodies. This process involves the physical adherence of dye molecules onto the surface of activated carbon particles, purifying the water. Moreover, the versatility of activated carbon allows for tailored adsorption processes, addressing specific dye types and concentrations. By mitigating water pollution caused by dyes, activated carbon plays a crucial role in environmental conservation efforts worldwide. Its application signifies a proactive approach towards safeguarding water resources and preserving aquatic ecosystems for future generations [1, 2].

## **I.2. Water pollution**

Water pollution is a physical, chemical, biological, or bacteriological degradation of its natural qualities, caused by human activities. It disrupts the living conditions of aquatic flora and fauna; it compromises water uses and the balance of the natural environment [3].

This is due to multiple and specific factors: discharges from industrial and agricultural activities and everyday human activities that occur in rivers, lakes, and seas. Pollution of an aquatic environment systematically has serious consequences [4].



## I.2.1 Sources of water pollution

Water pollution can occur from two sources:

- **Point source pollution**

When the source of water pollution is identified, such as pollutants entering the water from specific sources like ditches, pipes, industries, storm drains, and sewage treatment plants, it is referred to as point source pollution. This type of pollution can be distinguished from other sources [2].

- **Non-point source pollution**

When the source of water pollution is unknown or pollution originates from multiple diffuse sources, it is referred to as non-point source pollution. This type of pollution is challenging to control and may stem from various sources such as pesticides, fertilizers, and industrial wastes (Table I.1) [5].

**Table I.1:** Characteristics of point and nonpoint sources of chemical inputs to receiving waters [2].

Point Sources	Nonpoint Sources
<ul style="list-style-type: none"> <li>-Wastewater effluent (municipal and industrial)</li> <li>-Runoff and leachate from waste disposal sites</li> <li>-Runoff and infiltration from animal feedlots</li> <li>-Runoff from mines, oil fields, unsewered industrial sites.</li> <li>-Storm sewer outfalls from cities with a population &gt;100,000</li> <li>-Overflows of combined storm and sanitary sewers</li> </ul>	<ul style="list-style-type: none"> <li>-Runoff from agriculture (including return flow from irrigated agriculture)</li> <li>-Runoff from pasture and range</li> <li>-Urban runoff unsewered and sewer areas with a population &lt;100,000</li> <li>-Septic tank leachate and runoff from failed septic systems</li> <li>-Runoff from construction sites</li> <li>-Runoff from abandoned mines</li> <li>-Atmospheric deposition over a water surface</li> <li>-Activities on land that generate contaminants, such as logging, wetland conversion...</li> </ul>

### I.3. Dyes

#### I.3.1. Definition

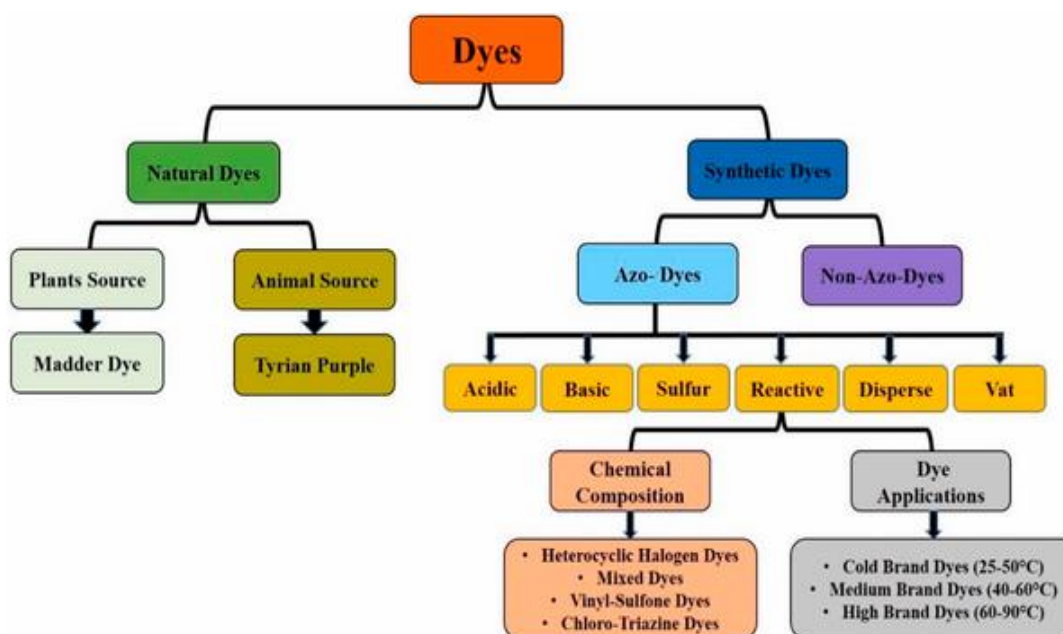
Dyes, colored chemical compounds, natural or synthetic, generally organic, which have the property of durably coloring the support on which they are applied. These compounds are used to color textiles, inks, paints, varnishes, food products, etc. Modern industrial terminology defines a colorant as a product containing pure organic dyes with various additives and blending agents to facilitate its use (Table I.2) [6].

**Table I.2:** Main chromophore and auxochrome groups, classified by intensity [7].

Chromophoric groups	Auxochroms groups <i>electrons donor groups</i>
Azo (-N=N-)	Amino (-NH <sub>2</sub> )
Nitroso (-N=O)	Methylamino (-NHCH <sub>3</sub> )
Carbonyl (=C=O)	Dimethylamino (-N(CH <sub>3</sub> ) <sub>2</sub> )
Vinyl (-C=CH <sub>2</sub> ) or methane (=Cn)	Hydroxyl (-OH)
Nitro (-NO <sub>2</sub> )	Alkoxy (-OR)
Thiocarbonyl (=CnS)	

#### I.3.2. Classification of dyes

Here's a basic classification of dyes into natural and synthetic categories, presented in (Figure I.1).



**Figure I.1 :** Dyes classification [8].

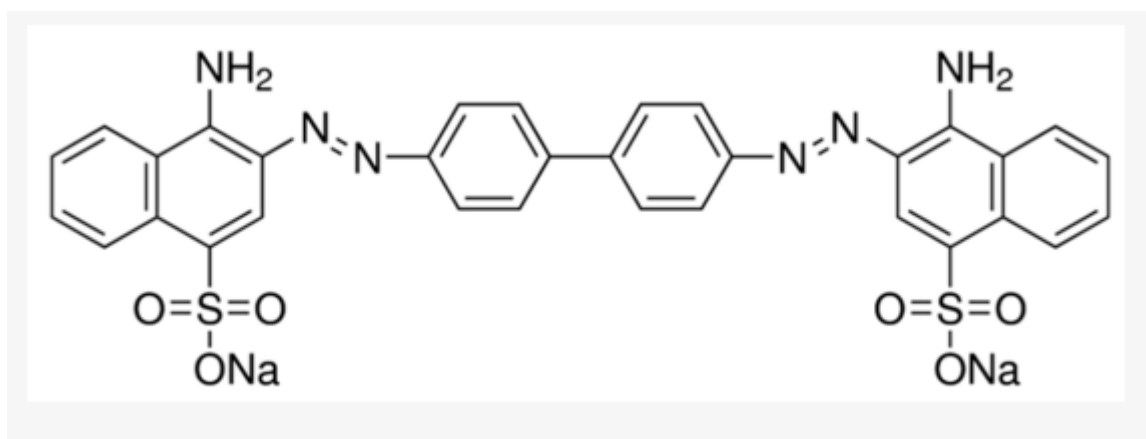
### I.3.3. Congo red

The Congo red dye poses as an organic pollutant that raises environmental concerns. It finds application in the textile, printing, dyeing, and rubber industries as a coloring agent. Due to its carcinogenic, mutagenic, and various other toxic effects on flora, fauna, and humans, there is a pressing need for the removal of CR from industrial wastewater heavily laden with CR [9].

➤ **Physic and chemical proprieties**

Congo red (CR) is an azo dye [10] (formula:  $C_{32}H_{22}N_6Na_2O_6S_2$ ; molecular weight: 696.66 g/mol. The Colour Index Number of CR is 22120 [11]. It is an anionic di-azo dye (contains two groups  $-N=N-$ ) composed of a sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid, known by common names such as CR 4B, C.I. 22120, Cotton red B, Cotton red C, Direct red 28, Cosmos red, Direct red Y, and Direct Red R [11, 10].

Congo Red is a synthetic dye belonging to the category of azo dyes. CR contains two azo ( $-N=N-$ ) chromophores and acidic auxochromes ( $-SO_3H$ ) linked with the benzene structures. CR is also called acidic diazo dye. A CR molecule exhibits linear symmetry, characterized by a hydrophobic core composed of two phenyl rings linked together by a di-azo linkage [10]. The phenyl rings are connected to two charged terminal naphthalene moieties containing sulfonic and amino groups. The chemical structure of CR is shown in Figure I.2, and it is made by mixing two molecules of naphthenic acid with tetrazotized benzidine [12].



**Figure I.2:** Molecular structure of CR [12].

### ➤ Toxicity

Because of its extensive usage, monitoring and controlling the adverse effects of any substance that could be potentially toxic is quite challenging. Nevertheless, a broad range of toxic effects have been noted with CR dye (Table I.3) [10].

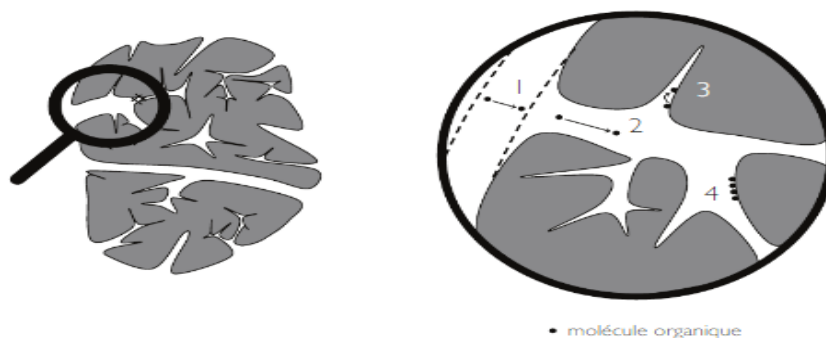
**Table I.3:** Toxic effects showed by (CR) and the affected targets [9, 10].

Order	Toxic/Inhibitory Effect	Affected Targets
1	Carcinogenic	Humans and animals
2	Mutagenic	Humans and animals
3	Causing infertility	Water flea ( <i>ceriodaphnia dubia</i> )
4	Increases COD	Water bodies and aquatic flora and fauna
5	It makes surface water unaesthetic	Water bodies
6	Allergic	Humans
7	Phytotoxicity	Plants

## I.4. Adsorption

### I.4.1. Definition

Adsorption is a surface phenomenon in which atoms, ions or molecules (adsorbate) (gas or liquid) can be organic or inorganic to adhere to the surface of a solid (adsorbent) from a gaseous phase, liquid or solid solution [13]. This phenomenon is very important in many physical and chemical processes: pollutant capture, gas separation, catalysis and so on. It is also the basis of many solid characterization methods, such as finite surface area measurement or porosity studies [14]. Depending on the interaction between adsorbate and adsorbent, we have physical adsorption or chemical adsorption, Explained in (Figure I.3) [15].



**Figure I.3:** The adsorption phenomenon inside an adsorbent grain [16].

### I.4.2. Types of adsorption

There are two types of adsorption: chemical adsorption (chemisorption) and physical adsorption (physisorption).

➤ **Chemical adsorption (chemisorption)**

Involves the formation of chemical bonds, which implies that the heat of adsorption is of the order of magnitude of the heats of reaction (200 to 400 KJ/mol). This type of adsorption is generally irreversible and occurs in a single layer (monolayer) [17, 18].

➤ **Physical adsorption (physisorption)**

In the case of physical adsorption, the attachment of adsorbate molecules to the adsorbent surface is essentially by Van der Waals forces. Physical adsorption occurs without modification of the molecular structure and is perfectly reversible (Table I.4) [19].

**Table I.4.** General characteristics of physisorption and chemisorption [20].

<b>Physisorption</b>	<b>Chemisorption</b>
-Weak interaction: electrostatic bond, -Van der Waals bond, hydrogen bond -Rapid reaction -Favored at low temperatures Low -activation energy -Reversible	-Strong interaction: covalent bond -complexation bond, ion exchange -Slow reaction -Favored at high temperatures -High activation energy -Irreversible difficult to reverse

### I.4.3. Adsorption kinetic models:

Predicting adsorption kinetics is an important step in the industrial design of adsorption columns. The nature of the adsorption process will depend on the physical or chemical characteristics of the adsorbent system, and also on the experimental conditions of that system.

The various kinetic models make it possible to predict the mechanism(s) involved in the adsorption process (adsorption to the surface, adsorption by chemical reactions and/or by diffusion mechanism) and the limiting stage of this process [21].

The most commonly used kinetic models are those of pseudo-first order (the Lagergren model), pseudo-second-order and diffusional models, shown in (Table I.5).

**Table I.5:** Adsorption kinetic models [22, 23, 24].

<b>Pseudo-first order</b> $(q_t = q_e(1 - e^{-k_1 t}))$	$k_1$ Velocity constant of the pseudo-first-order model (min <sup>-1</sup> );	[33]
	$q_e$ Equilibrium adsorption capacity (mg. g <sup>-1</sup> );	
<b>Pseudo-second ordre</b> $(q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t})$	$k_2$ Velocity constant of the pseudo-second-order (g mg <sup>-1</sup> . min <sup>-1</sup> );	[34]
	$q_e$ Equilibrium adsorption capacity (mg. g <sup>-1</sup> );	
<b>Intra-particle diffusion</b> $q_t = k_{diff}t^{0.5} + C$	$K_p$ Velocity constant of the diffusion Intra- particulate (mg (g .min <sup>0.5</sup> ) <sup>-1</sup> );	[35]
	$C$ Boundary layer thickness (mg. g <sup>-1</sup> );	

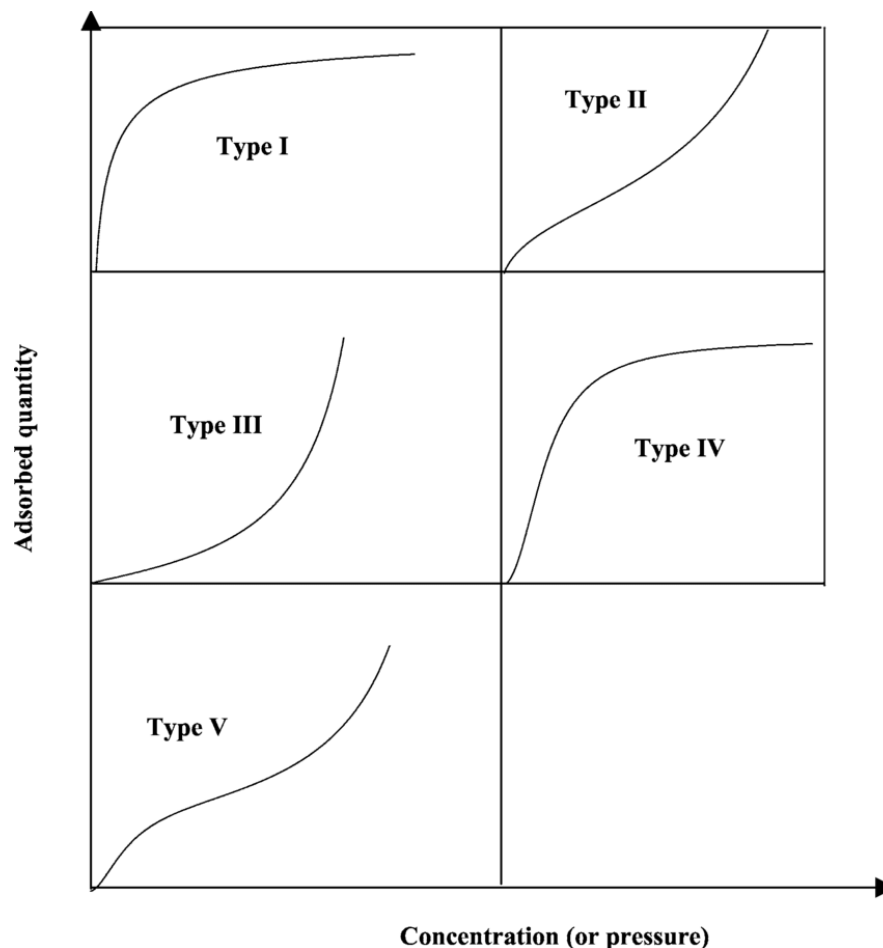
## I.4.4. Isotherm adsorption

### I.4.4.1. Classification of adsorption isotherms

Adsorption isotherms are specific to the adsorbent-adsorbate pair considered. Equilibria of adsorption, for a given temperature, are represented by graphs showing the quantity adsorbed ( $n_a$ ) on gram of solid adsorbent ( $m_s$ ) as a function of the equilibrium pressure  $P$  or the relative pressure  $P/P_0$ . The analysis of these isotherms allows for the determination of the porous structure of adsorbents. There are other types of isotherms, but the focus is on the most widespread ones. The main characteristics of these isotherms will be described as follows (Figure I.4) [25, 26 ,27, 28]:

- **Type I Isotherms:** These isotherms are obtained when the interaction between the adsorbent surface and the solute is lower than that between the solvent and the solute. The presence of already adsorbed molecules favors adsorption. The adsorbed molecules attract other molecules through Van Der Waals forces and pack together.
- **Type II Isotherms:** These isotherms present a cavity turned downwards, indicating that the more adsorption occurs, the more the number of free sites decreases. These isotherms are obtained when the force of attraction between the adsorbed molecules is weak. This phenomenon occurs when the interaction between the adsorbent surface and the solute is stronger than that between the solvent and the solute.

- **Type III Isotherms:** These isotherms have a nearly vertical part. At low concentrations of solute in the solvent, a significant amount of solute is adsorbed. This type of adsorption is obtained when the solute has a strong affinity with the adsorbent.
- **Type IV Isotherms:** These isotherms show a plateau at high pressures, indicating the saturation of the adsorbent. They are obtained with mesoporous adsorbents, and the adsorption is generally not reversible, with hysteresis between the adsorption and desorption isotherms.
- **Type V Isotherms:** These isotherms are characterized by weak adsorbent-adsorbate interactions with the presence of hysteresis. They are also obtained with mesoporous adsorbents.
- **Type VI Isotherms:** These isotherms are rare and are characterized by steps, indicating adsorption on a uniform surface.



**Figure I.4:** Different types of gas adsorption isotherms according to I.U.P.A.C [25,29].

## **I.5. Activated carbons**

### **I.5.1. Methods for producing activated carbon**

Activation methods for creating activated carbon vary, including steam, chemical, physical, oxidation, microwave, and electrochemical methods. These techniques induce pore formation within carbonized material, enhancing its surface area and adsorption capabilities. Each method offers distinct advantages and is selected based on factors like desired pore structure, production scale, and specific application requirements.

#### **➤ Chemical activation**

Chemical activation is another process used to obtain activated carbon [30]. That consists of impregnating the raw material with concentrated solutions of strongly oxidising agents such as acid, base or salt (e.g. sulphuric acid ( $H_2SO_4$ ), chloride, etc), zinc chloride ( $ZnCl_2$ ), or potassium hydroxide (KOH), etc.) to promote oxidation and/or dehydration. Then washed and dried. Activated carbon is thus obtained in a single step. Degree of impregnation of the material by the oxidant determines the final porous structure [31].

#### **➤ Physical activation**

Physical activation or partial gasification of carbon [32]. Consists of High-temperature oxidation of carbon (750 to 1000°C) using a low-oxidizing agent for oxidizing agent for 24 to 72 hours. The main gases used, alone or in mixtures, are air, water vapor and carbon dioxide. This process produces a narrow-pored coal, creating millions of microscopic cells alveoli on the surface of the carbon, dramatically increasing its surface area and adsorption capacity.

Temperature control is an important parameter, because above 1000°C, the reaction leads to material degradation. Below 800°C, however, the reaction is too slow or incomplete is too slow or incomplete, and therefore economically unattractive. In general, the activated carbons produced by this physical activation have a fine porous structure (narrow pores) [33].

### **I.5.2. Types of Activated Carbon**

Activated carbon comes in various types, each tailored to specific applications and manufacturing processes: Each type of activated carbon offers unique properties suited to different applications, and the selection of the appropriate type depends on factors such as pore size distribution, surface area, adsorption capacity, mechanical strength, and chemical compatibility with the target contaminants [34].



➤ **Powdered Activated Carbon (PAC)**

Finely ground activated carbon with particle sizes typically ranging from 5 to 150 micrometers. PAC is commonly used in water treatment, gas purification, and the food and beverage industry due to its high surface area and rapid adsorption kinetics.



**Figure I.5:** Powdered Activated Carbon (PAC) [35].

➤ **Granular Activated Carbon (GAC)**

Consists of larger granules, usually ranging from 0.2 to 5 millimeters in diameter. GAC is widely used in water and air purification systems, as well as in industrial processes like solvent recovery and gas phase applications, due to its excellent adsorption capacity and mechanical strength.



**Figure I.6:** Granular Activated Carbon (GAC) [35].

➤ **Extruded Activated Carbon**

Formed into cylindrical pellets or extrudates, extruded activated carbon offers enhanced mechanical strength and lower pressure drop compared to granular carbon. It is commonly used in gas phase applications, such as air purification and vapor phase adsorption.



**Figure I.7:** Extruded Activated Carbon [35].

➤ **Activated Carbon Fiber (ACF)**

Composed of fibers with diameters in the micrometer range, ACF offers a high surface area and excellent adsorption properties. It is used in various applications, including water purification, gas adsorption, and chemical filtration, where its unique structure provides efficient adsorption and ease of handling.



**Figure I.8:** Activated Carbon Fiber (ACF) [35].

### **I.5.3. Applications of Activated Carbon**

Activated carbon's versatility and effectiveness in adsorbing a wide range of substances make it indispensable in numerous fields, from healthcare to environmental protection [36].

➤ **Adsorption Power**

Activated carbon is exceptional at adsorbing pollutants, toxins, and impurities due to its high surface area and porous structure. This makes it a popular choice for various purification processes, including water and air filtration.

➤ **Water Purification:**

It's widely used in water treatment processes to remove organic compounds, chlorine, volatile organic compounds (VOCs), and other contaminants. You'll find activated carbon in everything from household water filters to large-scale municipal water treatment plants.

➤ **Air Purification**

In air purification systems, activated carbon can effectively remove odors, volatile organic compounds, and airborne chemicals. It's often incorporated into HVAC systems, air purifiers, and gas masks.

➤ **Medical and Pharmaceutical Uses**

Activated carbon is used in emergency medicine to treat certain types of poisoning by adsorbing the toxic substance in the gastrointestinal tract, preventing its absorption into the bloodstream.

➤ **Environmental Applications**

It's also utilized in environmental cleanup efforts, such as soil remediation and capturing pollutants from industrial emissions.

➤ **Industrial Processes**

Activated carbon plays a crucial role in various industrial processes, including gold recovery in mining, catalysis, and solvent recovery.

➤ **Renewable Energy**

It's even being explored for potential applications in renewable energy technologies, such as energy storage and carbon capture.

## **I.6. Characterization techniques**

### **I.6.1. Fourier transform infrared spectroscopy (FTIR)**

Fourier transform infrared spectroscopy is an analysis technique based on the absorption of infrared radiation by the material under analysis.

The absorption of infrared radiation by the material being analyzed. By detecting certain vibrations to determine the chemical functions present in the material.

When the energy supplied by the light beam is close to the vibration energy of the molecule, the latter will absorb it. The radiation and a decrease in the intensity reflected or transmitted intensity. The IR range between 4000 and 400  $\text{cm}^{-1}$  corresponds to the energy range of molecule vibrations. Not all vibrations give rise to absorption. Geometry of the molecule, and in particular its symmetry. For a given geometry, we can determine which modes of vibration are active in the infrared using group theory. The position of the absorption bands will depend in particular on bond strength and mass. Consequently, for a material with a given chemical composition and structure a set of characteristic absorption bands to identify it bands absorption [37].

### **I.6.2. Scanning electron microscopy (SEM)**

The working principle of an electron microscope dates back to 1932 when Ruska and Knoll first realized it. In this type of microscope, a focused electron beam is generated using a glow filament. These emitted electrons are then accelerated towards the sample. Upon collision with the sample, the electrons scatter back, and a detector measures the amount of this scattered electron. This process is repeated for each point on the sample, with the number of scattered electrons recorded for each point. Consequently, each point corresponds to a pixel in the microscopic image, with the brightness of each pixel representing the number of detected electrons. Thus, an electron microscope image is always grayscale [38].

### **I.6.3. Brunauer isotherm- Emette- Teller (BET)**

#### **I.6.3.1. Principle, measured and measurement**

The BET method is based on the physical adsorption/desorption of an inert gas on the sample surface.

BET-N<sub>2</sub> gas adsorption analysis is divided into two parts:

- The degassing phase, which aims to remove gas molecules and impurities initially adsorbed on the particle surface. This stage is carried out under vacuum, with initial heating to 90°C for 1 hour, then to 200°C for 12 hours (the degassing temperature must be adapted to the nature of the material under consideration).
- The analysis phase consists in measuring the quantity of gas adsorbed on the sample surface at each relative pressure point ( $P/P_0$ ). This is determined by the difference between the quantity of gas initially introduced and that remaining in the cell after adsorption. Adsorption/desorption isotherms are then plotted with the quantity of gas adsorbed (in cm<sup>3</sup>/g) as a function of relative pressure ( $P/P_0$ ). The amount of gas adsorbed is calculated for each relative pressure point over an interval of 0.01 to 0.99  $P/P_0$  [39].

#### I.6.4. UV-Vis Spectrophotometry

UV - Visible absorption spectroscopy is a quantitative analytical method based on the on the electronic transitions resulting from the absorption of light of a given wavelength. wavelength, it is used to measure the absorbance or optical density of a chemical substance chemical substance using substantially monochromatic light.

The UV spectroscopy range extends from  $\{\lambda = 200 \text{ nm} - 400 \text{ nm}\}$  but the visible light range from visible light from  $\{\lambda = 400 \text{ nm} - 800 \text{ nm}\}$ .

UV-Visible spectroscopy is performed using a spectrophotometer. When the cell containing the diluted sample of defined concentration to be analyzed is placed in a spectroscope, it receives radiation of intensity  $I_0$ , part of this incident light is absorbed absorbed ( $I_0$ ) and the rest transmitted ( $I$ ). The fraction of incident light absorbed by the substance analyzed substance contained in a cell of length  $l$  is given by Beer-Lambert's law [40].

$$A = \log (I_0/I) = \epsilon l C$$

- Where **A**: Absorbance formerly known as optical density (O.D.) (unit less).
- **I**: Intensity of transmitted light beam.
- **$I_0$** : Intensity of incident light beam.
- $\epsilon$  : Molar extinction coefficient (molar absorption coefficient) ( $\epsilon$  is in  $\text{L. mol}^{-1} \cdot \text{cm}^{-1}$ ), if  $C$  in  $\text{g/L}$  ( $\epsilon$  is in  $\text{L. g}^{-1} \cdot \text{cm}^{-1}$ ).
- **l**: Cell width (thickness) in cm.
- **C** : Solution concentration ( $\text{mol. L}^{-1}$ ).

UV-Vis spectroscopic data can give both qualitative and quantitative information about a compound or molecule under study. Regardless of whether quantitative or qualitative information is required, it is important to use a reference cell to zero the instrument for the solvent in which the compound is found. For quantitative information on the compound, calibrating the instrument using known concentrations of the compound in question in a solution with the same solvent as the unknown sample would be necessary. If the information required is simply proof that a compound is present in the sample being the sample being analyzed, a calibration curve will not be necessary; however, if a study or degradation reaction is underway and a concentration of the compound in solution is required, then a calibration curve is necessary [41].

**I.7. Conclusion**

In this theoretical chapter's conclusion, it's imperative to underscore the pivotal role of activated carbon in safeguarding water resources through adsorption. Activated carbon emerges as a cornerstone technology in combating pollution, offering a versatile and effective means of removing contaminants from water sources. Its ability to adsorb a diverse range of pollutants, including organic compounds, heavy metals, and emerging contaminants, underscores its significance in water treatment processes. By harnessing the inherent properties of activated carbon, we can mitigate the adverse effects of pollution on water quality, thus ensuring the sustainability of vital ecosystems and safeguarding public health. As we navigate the complexities of water management and environmental stewardship, continued research and innovation in activated carbon technology will remain indispensable in our quest to protect and preserve precious water resources for future generations.

**Bibliographic References**

- [1] ABDALLAH, Aziza, BOUGUERRA, Mouna, et SFAKSI, 2019. Elimination du chrome hexavalent Par adsorption sur le charbon actif obtenu à partir de liège. Thèse de doctorat. Université de Jijel.
- [2] SINGH, M. Romeo et GUPTA, Asha 2016. Water pollution-sources, effects and control. Centre for Biodiversity, Department of Botany, Nagaland University.
- [3] GEORGE Tchobanoglous, Franklin L Burton and H David Stensel. Metcalf & eddy, inc 2003. Wastewater Engineering : Treatment, Disposal, Reuse.
- [4] Z. I. E. FATMIA, « Analyse physico-chimique de l'eau de mer au niveau de quelques sites de rejets des eaux usées – Côte de Mostaganem », Université Abdelhamid Ibn Badis Mostaganem.
- [5] CHAUDHRY, F. Nn et MALIK, M. F 2017. Factors affecting water pollution: a review. J. Ecosyst. Ecography, vol. 7, no 1, p.1.
- [6] CAPON, Mady, COURILLEAU-HAVERLANT, Véronique, et VALETTE, Cécile 1993. Chimie des couleurs et des odeurs. Cultures et techniques.
- [7] LIN, Yao-Tung, WENG, Chih-Huang, et CHEN, Fang-Ying 2008. Effective removal of AB24 dye by nano/micro-size zero-valent iron. Separation and Purification Technology, vol. 64, no 1, p. 26-30.
- [8] <https://textileengineering.net/synthetic-dyes-properties-types-application/>
- [9] OLADOYE, Peter Olusakin, BAMIGBOYE, Mutiat Oyedolapo, OGUNBIYI, Olutobi Daniel, et al 2022. Toxicity and decontamination strategies of Congo red dye. Groundwater for Sustainable Development, vol. 19, p. 100844.
- [10] Sharf Ilahi Siddiqui, Esam S. Allehyani 3ORCID, Sami A. Al-Harbi 2023. Investigation of Congo Red Toxicity towards Different Living Organisms: A Review. Department of Chemistry , volume 11, issue 3.
- [11] YAKUPOVA, Elmira I., BOBYLEVA, Liya G., VIKHLYANTSEV, Ivan M., et al 2019. Congo Red and amyloids: history and relationship. Bioscience reports, vol. 39, no 1.
- [12] CLAVIJO, Camila et OSMA, Johann F 2019. Functionalized leather: A novel and effective hazardous solid waste adsorbent for the removal of the diazo dye congo red from aqueous solution. Water, vol. 11, no 9, p. 1906.
- [13] Arrob, Meriem 2023. Production du charbon actif par activation chimique de biomasse. Mémoire de master, Département de Science de la

- matière , Université Mohamed Khider de Biskra.
- [14] Ammari Meryem 2023. Conversion des déchets agricoles en charbon actif par activation chimique (Genévrier). Mémoire de master, Département de Science de la matière , Université Mohamed Khider de Biskra.
- [15] ZUE MVE Mexent, 2016. Préparation et caractérisation des charbons actifs obtenus à partir des coques de noix de Coula edulis: Application dans l'élimination en solution aqueuse des cations Mn (II) et Al (III) et des substances humiques. These de doctorat. Chimie des Matériaux-Inorganiques , Université des Sciences et Techniques de Masuku.
- [16] MERLE, Tony 2009. Couplage des procédés d'adsorption et d'ozonation pour l'élimination de molécules bio-récalcitrantes. Thèse de doctorat. Institut National des Sciences Appliquées de Toulouse.
- [17] CRINI, Grégorio, BADOT, Pierre-Marie, ROBERTS, George AF, et al 2009. Chitine et chitosane: du biopolymère à l'application. Presses Univ. Franche-Comté.
- [18] LANDOLT, Dieter 2003. Corrosion et chimie de surfaces des métaux. PPUR presses polytechniques.
- [19] M. lle MAMERI Imane 2017. Etude d'adsorption du rouge congo sur charbon actif préparé à partir des noyaux de jujube. Mémoire de master, Département de biologie. Université de Akli mohand oulhadj de Bouira.
- [20] ARRACHE Nor El Hodda Dr. DADOU Salima HALFAYA Sara Meriem mohammed HACENE 2022. Optimisation et Modélisation de l'élimination d'un polluant émergeant par l'adsorption sur l'argile brute. Mémoire de Master. Département de Génie des Procèdes. Université de BLIDA 1.
- [21] Y. Ho, J. Ng, & M. cKay 2000. Kinetics of pollutant sorption by biosorbents: review. Separation & Purification Reviews. Separation and Purification Methods, V29(2), P.189-232.
- [22] Y. S. Ho & G. Mckay 1999. The Sorption of Lead (II) Ions on Peat. Water Research, V33(2), P. 578-584.
- [23] ÖZACAR, Mahmut et ŞENGİL, İ. Ayhan 2004. Application of kinetic models to the sorption of disperse dyes onto alunite. Colloids and Surfaces A: Physicochemical and engineering aspects, , vol. 242, no 1-3, p. 105-113.
- [24] W.J. Weber, & IC. Morris 1963. Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division, V89(2), P. 31-60.



- [25] BENYABA Abdelkrim, ALIOUA Mostapha 2020. Adsorption isotherme et thermodynamique du colorant organique (Rhodamine B). Département des sciences de la matière. Université Ahmed Draia d'adjar.
- [26] [https://nte.mines-albi.fr/STP/fr/co/uc\\_IsothermeAdsorption.html](https://nte.mines-albi.fr/STP/fr/co/uc_IsothermeAdsorption.html)
- [27] FOLLIVI kloutse 2015. A yevidecaractérisation des matériaux adsorbants pour le stockage de l'hydrogène. mémoire de la maîtrise en sciences de l'énergie et des matériaux. l'université du québec à trois rivières.
- [28] [https://www.researchgate.net/figure/Differents-types-disothermes-dequilibre-dadsorption-en-phase-liquide-Giles-et-al\\_fig12\\_338680165](https://www.researchgate.net/figure/Differents-types-disothermes-dequilibre-dadsorption-en-phase-liquide-Giles-et-al_fig12_338680165).
- [29] Dermel.S, Medjedoub.D 2013. "Adsorption Du Colorant Rouge Sandocryl Par Les Déchets De Phosphates Algériens Beige Et Noir". Thèse De Master, Université A. Mira, Bejaïa.
- [30] C. M. Creanga, 2007. « Procédé AD-OX d'élimination de polluants organiques non biodégradables (par adsorption puis oxydation catalytique) ». Thèse pour l'obtention du grade de Docteur de l'Institut National Polytechnique de TOULOUSE.
- [31] <http://www.charbonactif.com>.
- [32] BOUCHELTA, Chafia, MEDJRAM, Mohamed Salah, BERTRAND, Odile, et al 2008. Preparation and characterization of activated carbon from date stones by physical activation with steam. Journal of Analytical and Applied Pyrolysis, vol. 82, no 1, p. 70-77.
- [33] BOUTADARA, Khadidja, BEN ALI, Lwiza, KALLOUM, Slimane, et al 2017. Valorisation des déchets ligno-cellulosiques, issus du palmier dattier, en charbon actif. Thèse de doctorat. Université Ahmed Draia-ADRAR.
- [34] H. Guedidi Ben Slama, 2005. « préparée dans le cadre d'une cotutelle entre l'Université de Grenoble et l'Université de Tunis El Manar », l'université de grenoble.
- [35] <https://nitsri.ac.in/Department/Chemical%20Engineering/BRTL11.pdf>
- [36] <https://sodimate-inc.com/activated-carbon-types-applications-advantages/>
- [37] AKOUCHE, Mariame 2016. Synthèse prébiotique de Ribonucléotides sur des surfaces minérales. Thèse de doctorat. Université Pierre et Marie Curie-Paris VI.
- [38] K. S. 2018. Subramanian. Textbook on Fundamentals and Applications of Nanotechnology, DAYA Publishing House, p 82.

- [39] GHOMRASNI, Najoua Bouzakher,2021. Identification et caractérisation métrologique des nanoparticules en matrices complexe. Thèse de doctorat. Université Paris-Saclay.
- [40] Chebaki, Rachid,2023. Synthèse, Caractérisation et étude computationnelle des composés hétérocycliques à intérêt biologique. Thèse de doctorat, Université de Mohamed Kheider Biskra.
- [41] BROWN, J. Quincy, VISHWANATH, Karthik, PALMER, Gregory M., et al 2009. Advances in quantitative UV–visible spectroscopy for clinical and pre-clinical application in cancer. Current opinion in biotechnology, vol. 20, no 1, p. 119-131.

# *Chapter II*

*Methods, Results and*

*Discussions*

## II.1. Introduction

In this chapter, we focus on the complex process of creating two activated carbons from agricultural waste, with the emphasis on Ziziphus Lotus seeds, so that they have specific textures and characteristics.

The methodology is based on chemical activation using sodium hydroxide. This technique was chosen for its effectiveness in activating the raw material derived from agricultural waste, thus improving its ability to adsorb a dangerous dye that is Congo Red and its reactivity on the surface of the charcoal.

The chapter also looks at the characterisation of activated carbons. Using various analytical techniques such as spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface analysis, we seek to obtain a comprehensive understanding of their structural, morphological and textural properties.

In addition, we are evaluating the performance of activated carbons in removing Congo red, a widely used pollutant dye, from aqueous solutions. This evaluation provides an overview of the adsorption efficiency and the ability of the activated carbons produced to attack environmental contaminants.

## II.2. The raw material (ziziphus Lotus seeds)

Ziziphus Lotus is a deciduous shrub or small tree belonging to the Rhamnaceae family. It is native to the mediterranean region, particularly found in areas with a dry and warm climate, including parts of Europe, North Africa, and Asia Minor. The Lotus Ziziphus typically grows up to 5-10 meters in height, with a spreading, thorny canopy. Its leaves are glossy green and ovate to oblong in shape, with serrated margins. The flowers are small, greenish-yellow, and inconspicuous, blooming in clusters from spring to early summer [1].

The plant produces small, round fruits that resemble olives in appearance, are edible and have a sweet, apple-like flavor when fully ripe, fruits contain anthraquinone glycosides, making them very rich in vitamins, particularly vitamin C, vitamin B, and glycosides and flavonoids [2].

In addition to its culinary uses, Ziziphus Lotus has been historically valued for its medicinal properties. Various parts of the plant, including the fruits, leaves, and bark, have been used in traditional medicine to treat ailments such as digestive disorders, insomnia, and respiratory conditions [3].

With the aim of valorizing local by-products, we used the fruit seeds of the Rhamnus tree from the Biskra region as a precursor. These agricultural residues are abundantly available in Algeria.



**Figure II.1:** Ziziphus Lotus tree and its fruits.

### II.3. Synthesis of activated carbons

In this study, we prepared two types of activated carbons, both through chemical activation using sodium hydroxide. However, they differed in the presence of a precarbonization step.

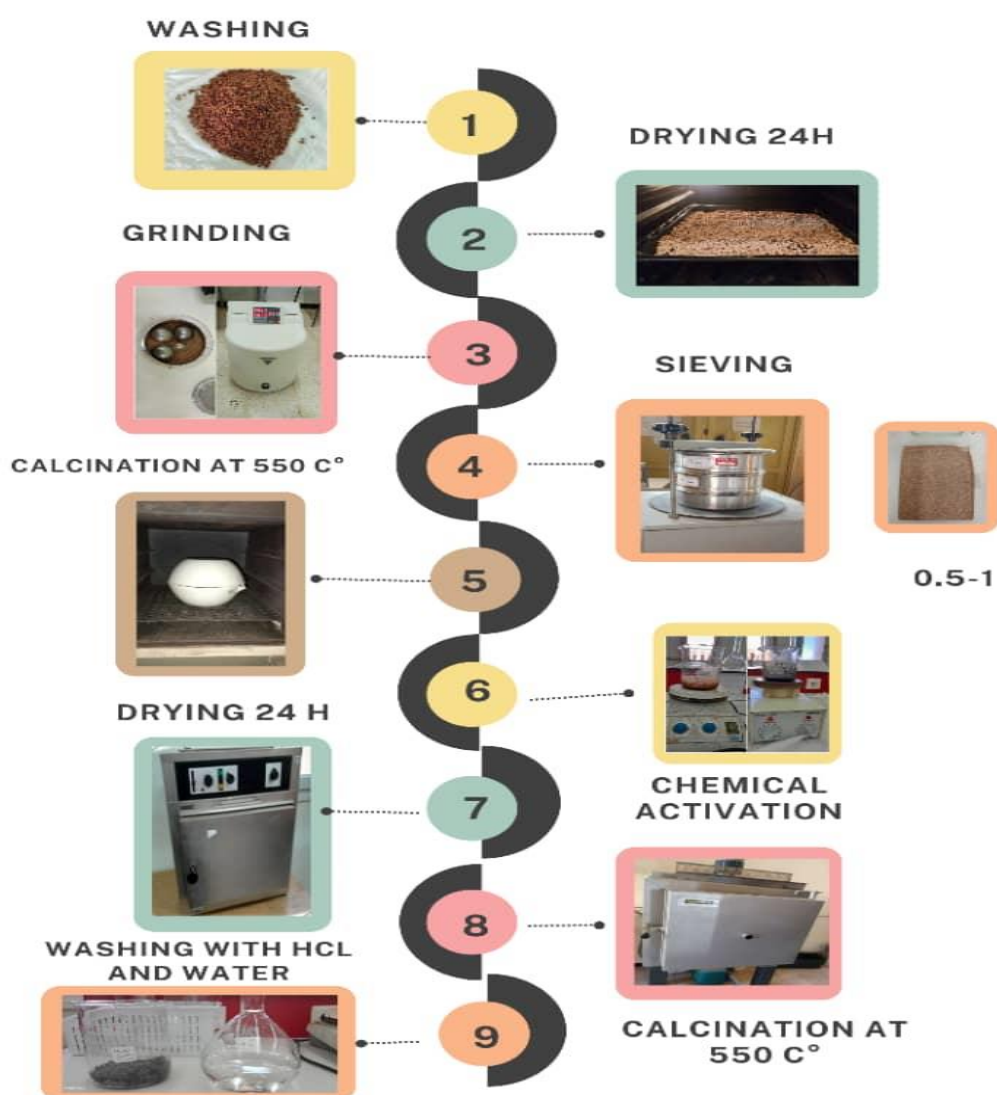
The two activated carbon utilized Lotus Ziziphus seeds as the precursor material and involved a precarbonization step prior to chemical activation. This step was crucial for adjusting the properties of the precursor material before the chemical activation process.

In contrast, the second activated carbon was produced without a precarbonization step, directly subjecting the precursor material to chemical activation with sodium hydroxide. By comparing these two approaches.

By comparing these two approaches, we aimed to assess the influence of precarbonization step on the properties of the resulting activated carbons. Thereby gaining insights into the optimization of the activation process for specific applications such as the adsorption of the dangerous dye Congo Red from aqueous solutions.

### II.3.1. Preparation of activated carbon (AC1)

The synthesis procedures for activated carbons (AC1) is depicted in Figure II.2, providing a visual overview of the production process. This schematic diagram outlines the key steps involved in the synthesis, offering a clear understanding of the sequential stages.



**Figure II.2:** Activated carbon (AC1) preparation protocol.

Each stage of the synthesis process, from precursor preparation to activation and characterization, is depicted sequentially, offering a comprehensive visual guide to the production process.

### ➤ Washing seeds

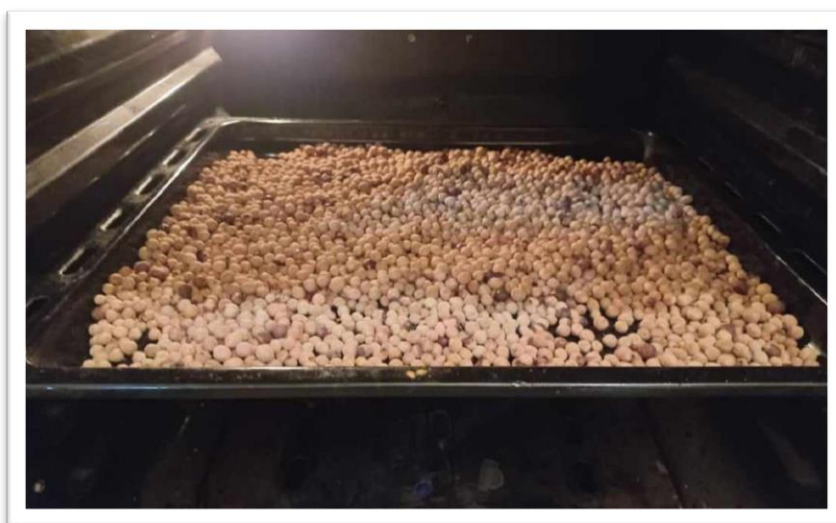
Washing the seeds with tap water is the initial step, followed by rinsing with distilled water to eliminate impurities thoroughly. This dual washing process ensures the removal of contaminants from the seeds, preparing them for subsequent stages of the procedure, as show in Figure II.3.



**Figure II.3:** Washed Ziziphus seeds.

### ➤ Drying

Placing the seeds into crucibles, they are dried inside the oven for 24 hours. The temperature is set at 110°C to facilitate the drying process effectively, as observe in Figure II.4.



**Figure II.4:** Oven-dried seeds.

### ➤ Grinding

The cores undergo crushing using a mechanical grinder. This process results in particles of varying sizes, essential for achieving the desired texture, as it turns out Figure II.5.



**Figure II.5:** Grinders and the grinded seeds.

### ➤ Sieving

At this stage, following the crushing process, we utilize a sieve shaker equipped with two sieves one with a diameter of 0.5 mm and another with a diameter of 1 mm. This enables the separation of the crushed material into pellets with a diameter ranging between 0.5 mm and 1 mm, as highlighted by Figure II.6.



**Figure II.6:** Sieving machine.



### ➤ Precarbonization

Is a crucial step in the production process of activated carbon, serving to convert the raw material into carbon. This transformation occurs within an oven, where the material is subjected to a temperature of 550°C for a duration of 1 hour. The heating rate is carefully controlled at 10°C/minute to ensure uniform heating throughout the material. Through this controlled heating process, the precursor material undergoes thermal decomposition, resulting in the formation of carbonaceous residues. This precarbonization step is essential for removing volatile components and stabilizing the material, laying the foundation for subsequent activation processes to enhance the material's adsorption properties, as show in Figure II.7.



**Figure II.7:** Calcining the pellets product in the oven.

### ➤ Chemical activation

The granules underwent chemical activation using NaOH, following this procedure: The grains were soaked in a sodium hydroxide NaOH solution at a weight ratio of 1:1 at ambient temperature for 6 hours while being stirred. Subsequently, they were filtered and dried in an oven at 105°C for a duration of 24 hours, as observe in Figure II.8 [4].



**Figure II.8:** Impregnated granules.

➤ **carbonization (Calcination)**

Exposing the material to a temperature of 550°C. Likewise, the heating rate remains constant at 10°C per minute to guarantee uniform heating across the material. This meticulously controlled thermal process is essential for advancing the carbonization of the initial material, aiding in the transformation of any remaining carbonaceous elements into a more resilient carbon framework, as it turns out Figure II.9.



**Figure II.9:** Calcining the pellets product in the oven (Second time).

### ➤ Washing with HCl Solution and with water

Activated carbon in its crude form undergoes a washing process to eliminate any residual sodium hydroxide NaOH by treating it with hydrochloric acid (HCl) solution. The material is then rinsed with distilled water until reaching a neutral pH of 7. Following this, the activated carbon is dried in an oven at 110°C for a duration of 24 hours. Finally, it is stored for further use in subsequent processes or applications, as highlighted by Figure II.10.



**Figure II.10:** Activated carbon washed with HCl and water with pH measurement.

## II.3.1.1. Results and discussion

### II.3.1.1.1. Fourier transform infrared spectroscopy (FTIR)

The surface functional groups of AC1 were identified by Fourier transform infrared spectroscopy using an FTIR-8400s SHIMADZU., Shimadzu, operating in the range of 4000-400  $\text{cm}^{-1}$  and employing the KBr pellet method. Our samples for analysis come in pellet form. They are prepared by mixing 0.2 g of KBr and 0.001 g of the sample, which is ground in an agate mortar and then compressed by a hydraulic press, as show in Figure II.11 end Figure II.12.



Figure II.11: pellet preparation.



Figure II.12: Fourier transform infrared spectrometer FTIR- Shimadzu FTIR-8400.

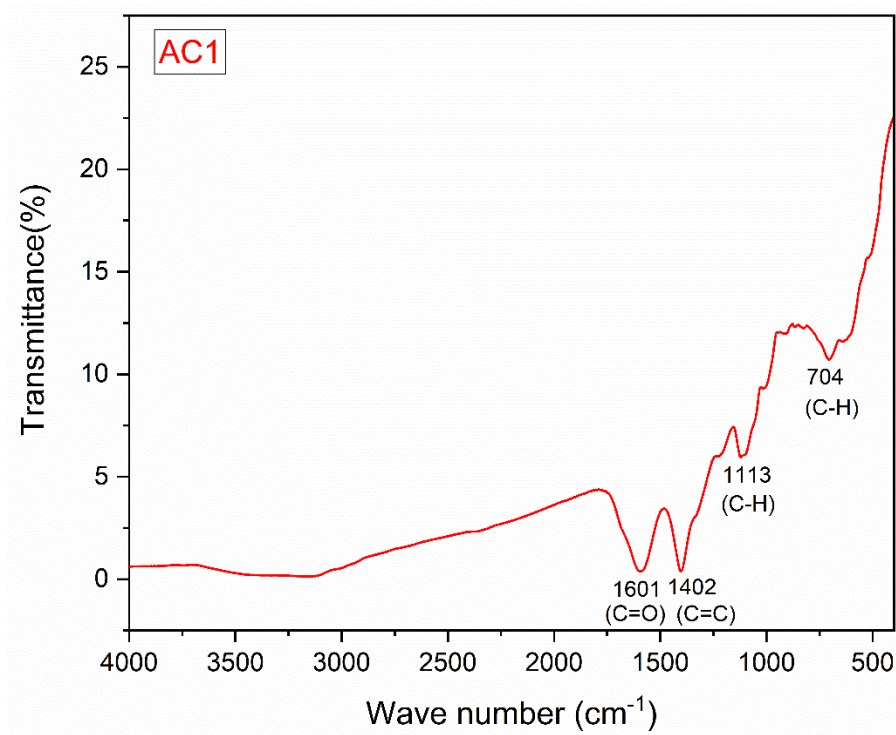


Figure II.13: Infrared spectrum of activated carbon (AC1).

The region of the spectrum of  $1601\text{ cm}^{-1}$  is attributed to axial deformation of carbonyl groups (C=O). The stretching vibration of the molecular plane of (C=C) bonds, characteristics of aromatic rings appear in the region of  $1402\text{ cm}^{-1}$ . The region between  $704$  and  $1113\text{ cm}^{-1}$  contains various bands related to aromatic, out of plane (C-H) bending with different degrees of substitution [5, 6].

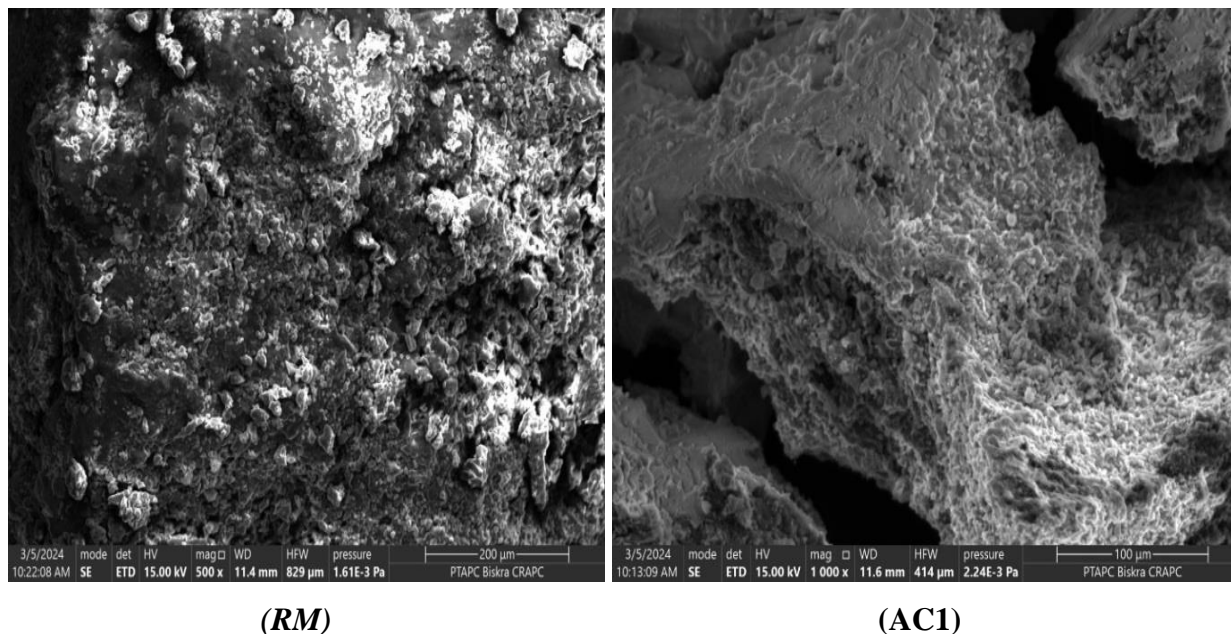
### **II.3.1.1.2. Scanning electron microscopy Surface morphology (SEM)**

Scanning electron microscope (SEM) analysis was performed to examine the presence of porosity and the surface morphology.

Figure II.14 presents a typical SEM image of the prepared activated carbon, displaying particles with irregular shapes and visible cavities. These cavities result from the chemical treatment of the precursor with NaOH during the preparation process. Using NaOH as an activating agent offers multiple advantages, including low energy consumption and a high yield of activated carbon. During the activation process, NaOH serves as a catalyst, penetrating the biomass structure and acting as a template, leading to the formation of porous activated carbon.

After high temperature carbonization and NaOH activation, the produced AC1 had a rough surface with dense pores, which might be due to the volatilization of volatile compounds and gas components at high temperatures, and the further rupture of cell walls caused by NaOH erosion [7].

These photographs show the difference between the pores and structure of two compounds: raw material and AC1 activation carbon. Overall, the raw material (RM) has a smooth, textured structure characterized by long, narrow grooves on the surface and minimal porosity. In contrast, the pores in AC1 are of various shapes and larger diameters, highlighting the effectiveness of the activation process.



**Figure II.14:** SEM photograph of the raw material (RM ) and activated carbon (AC1).

The results of EDS analysis indicate that RM contains an average proportion of atomic carbon (58.48%), which means that this raw material is a particularly suitable activated carbon precursor. On the other hand, this analysis shows that sample AC1 has a high carbon content with an atomic fraction of carbon of (83.51%). This indicates that the two carbonisation steps and the activating agent NaOH are suitable dehydrating agents and that the sample is almost carbonised.

### II.3.1.1.3. Textural characterization

The experiment utilized a Micromeritics ASAP 2010 instrument for physical adsorption. Nitrogen gas was employed as the analysis medium at a temperature of  $-196.011^{\circ}\text{C}$ . The isotherm was meticulously created by incrementally introducing and removing precise gas quantities, ensuring equilibrium at each relative pressure point ( $P/P_0$ ), where  $P_0$  represents the saturation pressure at  $-196.011^{\circ}\text{C}$ . The specific surface area of the synthesized AC1 was determined using the Brunauer-Emmett-Teller (BET) method.

The specific surface area ( $S_{\text{BET}}$ ) is given by the following equation:

$$S_{\text{BET}} = V_m L \sigma / V_0$$

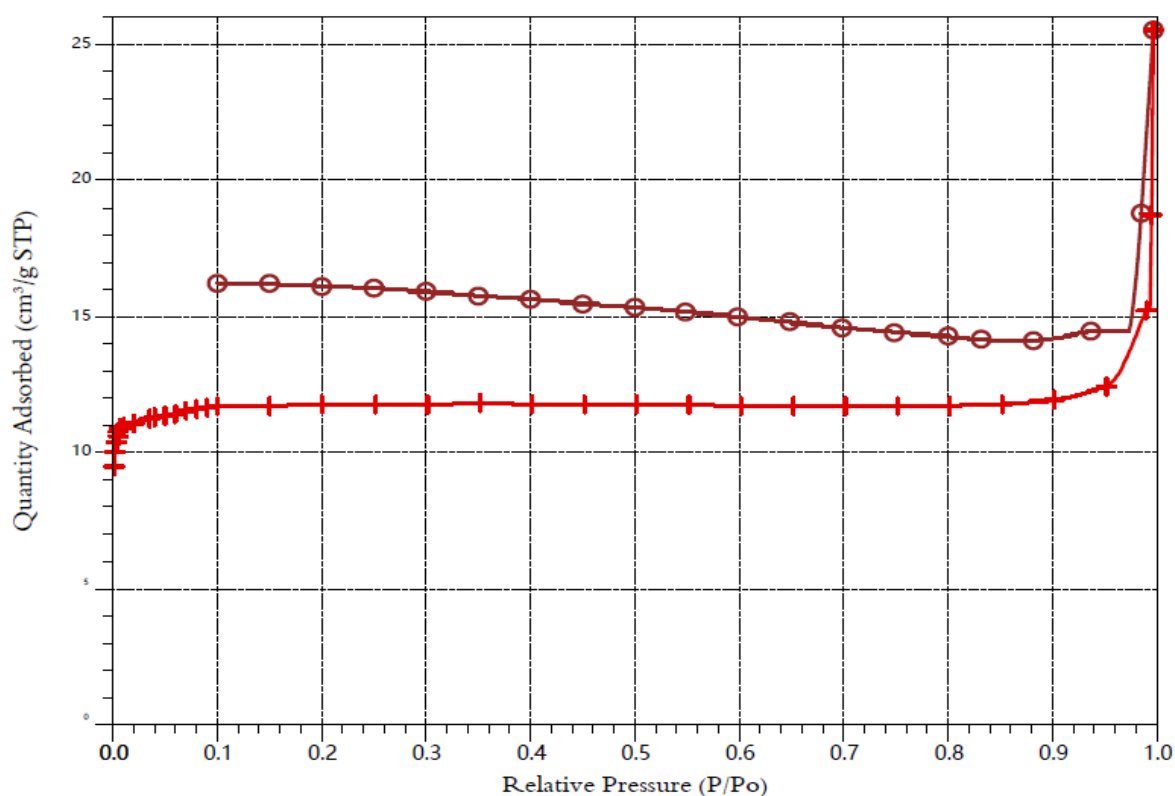
Where:

- $V_m$  is the monolayer capacity ( $\text{cm}^3/\text{g}$ ) at STP ( $T=0^{\circ}\text{C}$ ,  $P=1\text{ atm}$ ).
- $V_0$  is the molar volume of nitrogen, supposed as an ideal gas ( $22414\text{ cm}^3.\text{mol}^{-1}$  at STP).

- $L$  is the Avogadro constant.
- $\sigma$  is the molecular cross-sectional area (for nitrogen,  $\sigma = 0.162 \text{ nm}^2$  at  $-196.011 \text{ }^\circ\text{C}$ ).

Figure II.15 illustrates the nitrogen adsorption-desorption isotherms of the synthesized AC1. According to the IUPAC classification, the isotherm resembles a Type II isotherm, it describes adsorption on weakly porous surfaces. This type of isotherm occurs in multilayer adsorption. The inflection point of the curve indicates that the first layer is fully saturated, and consequently, multilayer adsorption can occur as the relative pressure increases[8].

This result suggests that the specific surface area of AC1, as determined by the BET method, is  $37.6432 \text{ m}^2/\text{g}$ . However, this value appears to be on the lower end when compared to activated carbons produced using chemical activators such as  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$ [9, 10]. In other words, AC1 may not have as much exposed surface area for adsorption compared to those activated carbons synthesized with these chemical activators.



**Figure II.15:** The Nitrogen adsorption-desorption isotherms at  $-196,011 \text{ }^\circ\text{C}$  of AC1.

#### II.3.1.1.4. CR adsorption on the synthesized (AC1) under optimized conditions

The classic experimental methodology involves fixing the levels of all variables except one and measuring the system's response for different values of the variable in question. This approach requires conducting a significant number of trials. For many problems, conducting such a large number of experiments is challenging. Therefore, the issue is to find a tool or method to reduce the number of experiments without sacrificing precision. The methodology of experimental design allows achieving this objective. In this context, experimental design can be defined as the science of organizing (or planning) experimental trials and modeling the resulting data [11].

A stock solution of CR with a concentration of 100 mg/L was prepared by mixing an appropriate amount of solid CR with distilled water. The stock solution was then appropriately diluted with distilled water to achieve the desired initial concentrations. Adsorption tests were conducted using varying amounts of AC1 ranging from 1g/l to 5 g/l, in 50 mL of the CR solution. The contact time between CR molecules in solution and AC1 grains varied between 20 minutes and 120 minutes. Moderate agitation was maintained to ensure good contact between the adsorbent and the adsorbate. The experimental setup used is illustrated below, as observe in Figure II.16 [12].



**Figure II.16:** The experimental setup used for CR adsorption on the synthesized AC1 under optimized conditions.



The quantity of interest is the adsorption rate of CR (yield (%)), which is defined by the formula:

$$R(\%) = [(C_0 - C_e) / C_0] \times 100$$

Where  $C_0$  and  $C_e$  represent respectively the initial and equilibrium concentrations of CR (mol/L). The aim of this study is to identify the influential factors, as well as their interactions, on the retention capacity of the considered adsorbent. To this end, our focus has been on the investigation of three factors, namely:

- Factor 1 ( $x_1$ ): Initial concentration of CR ranging from 10 mg/l to 50 mg/l
- Factor 2 ( $x_2$ ): Contact time varying in the range of 20 minutes to 120 minutes.
- Factor 3 ( $x_3$ ): Mass of the adsorbent varying in the range of 1 g/l to 5 g/l

The analysis of residual concentrations was conducted using UV-Visible spectrophotometry PerkinElmer UV/VIS Spectrometer Lambda.



**Figure II.17:** UV-Visible spectrophotometry PerkinElmer UV/VIS Spectrometer Lambda.

The factors in centered reduced coordinates as well as the main effects and their interactions are grouped in the tables below.

**Table II.1:** Matrix of main effects (AC1).

Run	Facteur 1 ( $x_1$ ) C (mg/l)	Facteur 2 ( $x_2$ ) Time (min)	Facteur 3 ( $x_3$ ) Dose (g/l)
1	10	70	1
2	10	20	3
3	30	20	1
4	30	70	3
5	10	70	5
6	50	20	3
7	30	120	1
8	30	70	3
9	50	120	3
10	10	120	3
11	30	20	5
12	30	120	5
13	50	70	5
14	50	70	1

The optimization operation for the first-degree model with interaction is performed in Matlab using the optimization command `fmincon`.

The optimal conditions obtained are: 4 grams of activated carbon AC1, stirring for 1 hour. This implies that to achieve maximum retention efficiency of CR by activated carbon AC1, this configuration will yield a maximum efficiency of 60%.

### II.3.2. Preparation of activated carbon (AC2)

We prepared AC2 in the same way as AC1 without the Calcination step as shown in the diagram below Figure II.18.

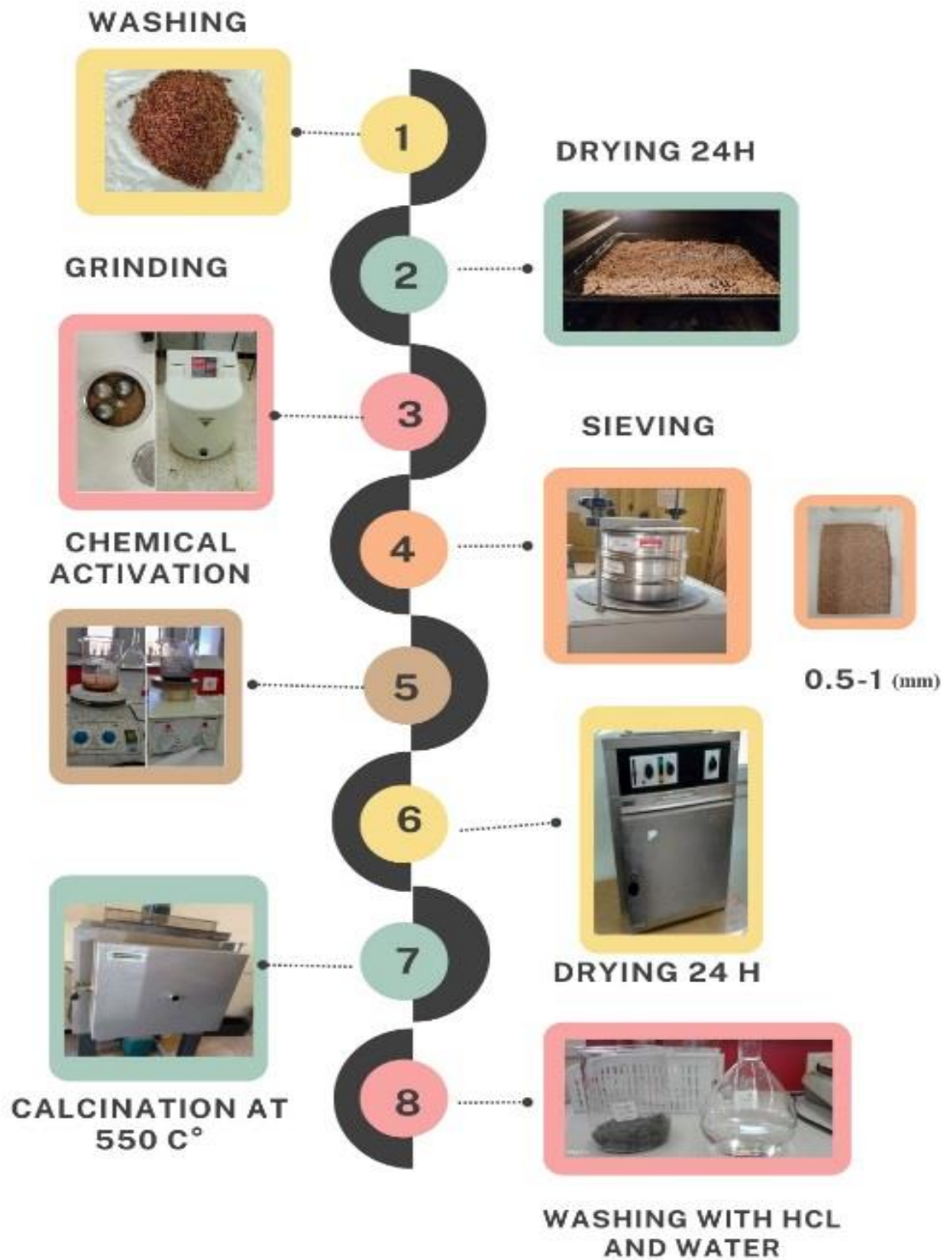


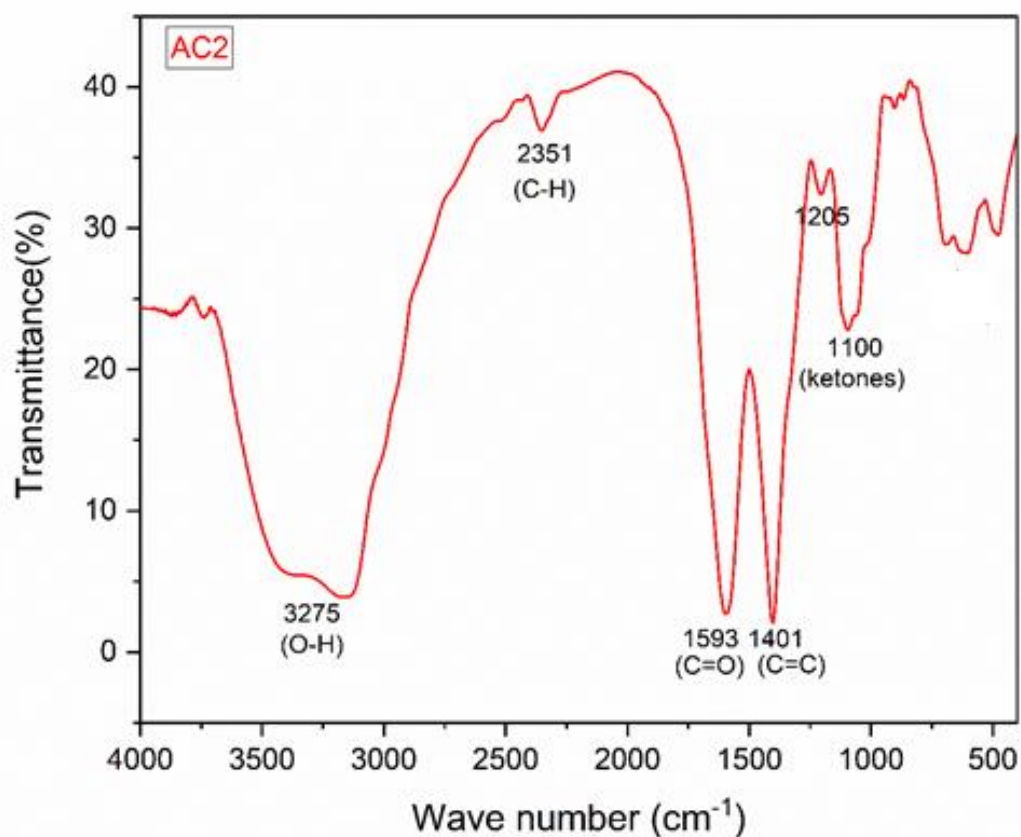
Figure II.18: Activated carbon (AC2) preparation protocol.

### II.3.2.1. Results and discussion

#### II.3.2.1.1. Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectra were obtained to evaluate qualitatively the shown in Figure II.19. shows the FTIR spectrum of AC2, which indicated various surface functional groups.

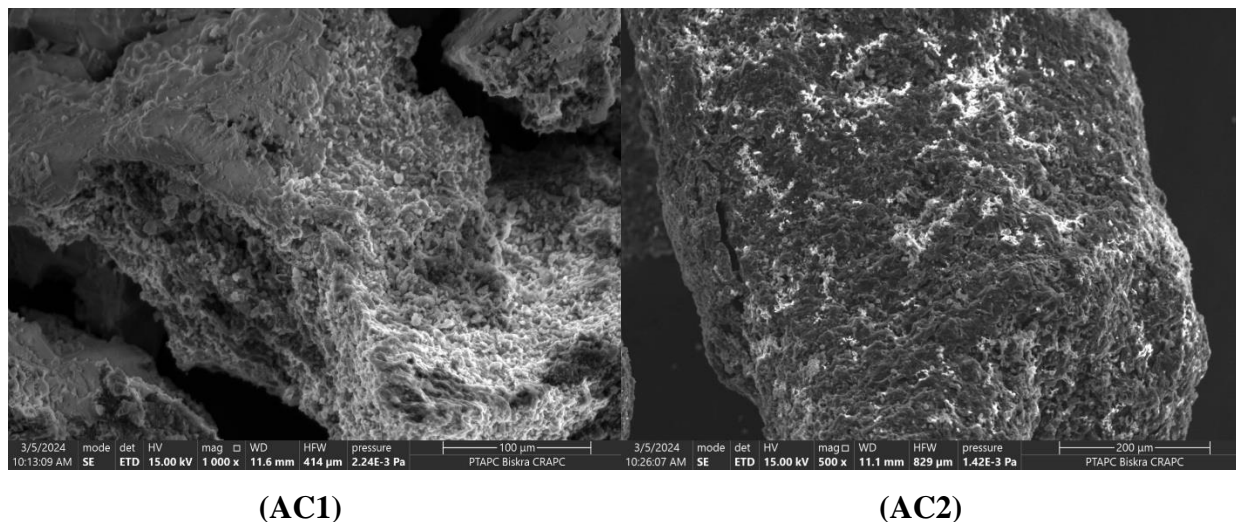
The bands at  $3275\text{ cm}^{-1}$  can be assigned to (O–H) stretching of hydroxyl groups or adsorbed water. The band located at around  $2351\text{ cm}^{-1}$  corresponds to (C–H) stretching vibration of aliphatic carbon or due to  $\text{CH}_2$  of  $\text{CH}_3$  deformation. The region of the spectrum of  $1593\text{ cm}^{-1}$  is attributed to axial deformation of carbonyl groups (C=O). The stretching vibration of the molecular plane of (C=C) bonds, characteristics of aromatic rings appear in the region of  $1401\text{ cm}^{-1}$ . Axial and angular deformation of ketones arises in the region of  $1205\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ [5,6].



**Figure II.19:** Infrared spectrum of activated carbon (AC2).

### II.3.2.1.2. Scanning electron microscopy (SEM)

SEM examination is intended to illustrate porosity of AC2, especially that decreased by the elimination of precarbonization step. porosity decreases the carbon's specific surface area and, consequently, the number of active sites, as highlighted by Figure II.20 [13].

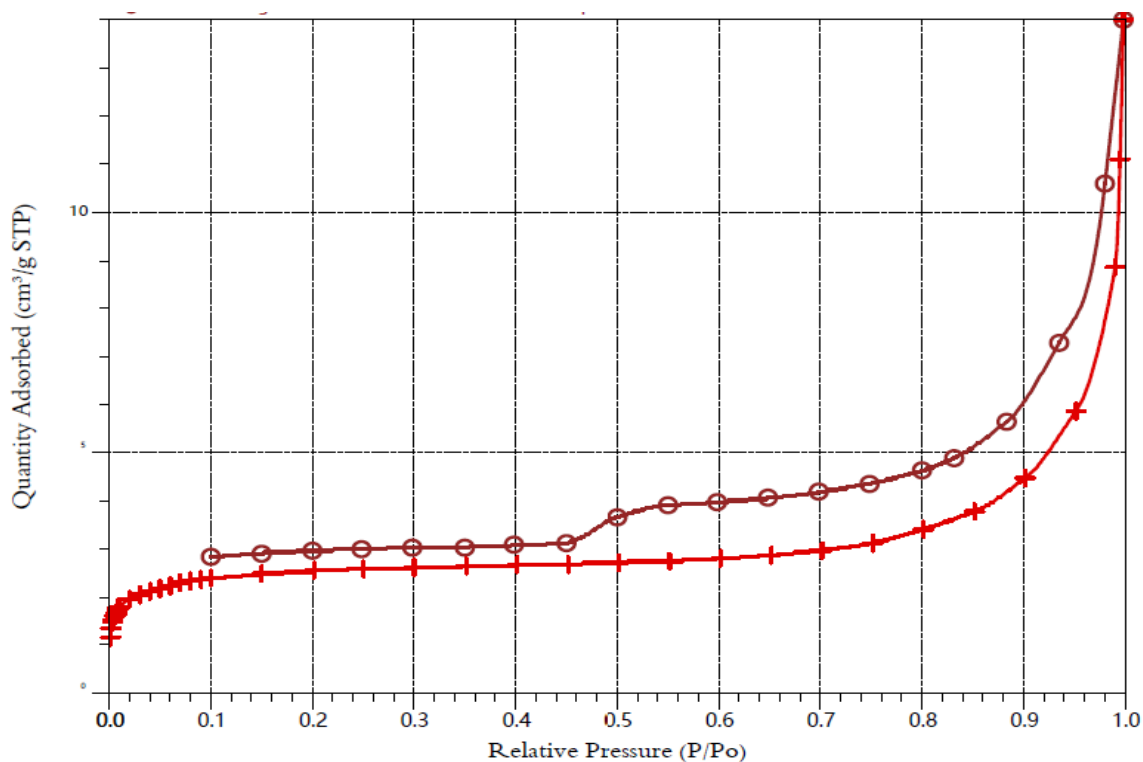


**Figure II.20:** SEM images of Activated Carbons (AC1) and (AC2).

### II.3.2.1.3. Textural characterization of (AC2)

The experiment employed a Micromeritics ASAP 2010 instrument for physical adsorption, utilizing nitrogen gas as the analysis medium at  $-196.011^{\circ}\text{C}$ . The isotherm was carefully generated by incrementally adding and removing precise amounts of gas, ensuring equilibrium at each relative pressure point ( $P/P_0$ ), with  $P_0$  representing the saturation pressure at  $-196.011^{\circ}\text{C}$ . The specific surface area of the synthesized AC2 was determined using the Brunauer-Emmett-Teller (BET) method. This finding indicates that the specific surface area of (AC2), as measured by the BET method  $9.7211 \text{ m}^2/\text{g}$ .

According to the IUPAC isotherm classification, characteristics of type II isotherms. When the relative pressure  $P/P_0$  (0-0.1) was low, the adsorption amount of  $\text{N}_2$  increased rapidly, which might be due to the adsorbent interaction promoting the gas molecules to fill the micropores, as show in Figure II.21[14].



**Figure II.21:** The Nitrogen adsorption-desorption isotherms at  $-196,011\text{ }^{\circ}\text{C}$  of AC2.

#### II.3.2.1.4. CR adsorption on the synthesized AC2 under optimized conditions

To optimise the adsorption phenomenon for AC2, we followed the same procedure as for AC1, taking into account the particularities of the materials used and the experimental conditions, in order to maximise adsorption and obtain reliable and reproducible results.

The optimal conditions obtained are: 3.5 grams of activated carbon AC2, stirring for 2 hour. This implies that to achieve maximum retention efficiency of CR by activated carbon AC1, this configuration will yield a maximum efficiency of 70%.

## II.4. Conclusion

This chapter has detailed the successful preparation of activated carbons from Ziziphus Lotus seeds through chemical activation with NaOH, followed by their application in the removal of a reactive dye, Congo Red. The activated carbons, designated as AC1 and AC2, were synthesized using two different preparation methods. Their structural and textural properties were thoroughly characterized using a combination of N<sub>2</sub> adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The BET surface area analysis revealed significant surface areas for both activated carbons, with AC1 exhibiting a surface area of 37.6432 m<sup>2</sup>/g and AC2 showing an even higher surface area of 9.7211 m<sup>2</sup>/g.

The adsorption performance of the activated carbons was evaluated by examining the effects of various parameters, including initial dye concentration, contact time, and activated carbon mass,

The study underscores the potential of AC1 and AC2 as effective adsorbents for dye removal from wastewater. AC1, in particular, stands out as a cost-effective solution due to its adequate surface area and substantial adsorption capacity. The ability of these activated carbons to remove Congo Red dye efficiently highlights their applicability in treating industrial effluents and mitigating environmental pollution.

**Bibliographic References**

- [1] Site web: <https://www.mnhn.fr/fr/jujubier-commun>
- [2] <https://www.mnhn.fr/fr/jujubier-commun>
- [3] [https://www.persee.fr/doc/jatba\\_0370-5412\\_1947\\_num\\_27\\_301\\_6125](https://www.persee.fr/doc/jatba_0370-5412_1947_num_27_301_6125)
- [4] B. Brahim, D&W. Souaci 2021. Enquête ethnobotanique et étude phytochimique de deux plantes médicinales (*Rosmarinus officinalis* et *Juniperus phoenicea*), dans la région d'oued souf. Université constantine, Mémoire de Master Académique.
- [5] André L. Cazetta, Alexandro M.M. Vargas, Eurica M. Nogami 2011. NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption", *Chemical Engineering Journal*. p121.
- [6] OUIKENE Samir, CHEMEUR Nawel 2015. Etude comparative entre un adsorbant utilisé à la station de traitement des eaux de Taksebt et des adsorbants préparés à base de grignon d'olive. mémoire de master, département de chimie de l'environnement, université Mouloud Mammeri Tizi Ouzou.
- [7] Lin L, Zhai S-R, Xiao Z-Y, Song Y, An Q-D and Song X-W 2013. Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks *Bioresour. Technol* **136** 437–43.
- [8] C. E. Chitour, 2004. *Physico-chimie des surfaces*, 2ème Ed. Augmentée, Office des publications universitaire, Alger.
- [9] BEN ABDALLAH. Zoubir, HOUHOUNE. Mustapha 2021. Valorisation des déchets agricoles par production du charbon actif, mémoire de master. Sciences de la matière Chimie, Chimie du matériaux. Université Mohamed Khider de Biskra.
- [10] Ammari. Meryem 2023. Conversion des déchets agricoles en charbon actif par activation chimique (Genévrier). Mémoire de master, Département de Science de la matière, Université Mohamed Khider de Biskra.
- [11] Dounia zed, Merabet 2017. Optimisation sous contraintes du rendement de l'adsorption de polluants organiques. Mémoire de Master, Département des Sciences de la Matière, Université M. Khider de Biskra.
- [12] Raj R A, Manimozhi V and Saravanathamizhan R 2019. Adsorption studies on removal of Congo red dye from aqueous solution using petroleum coke *Pet. Sci. Technol.* **37** 913–24.
- [13] Doke K M, Yusufi M, Joseph R D and Khan E M 2016. Comparative Adsorption of Crystal Violet and Congo Red onto ZnCl<sub>2</sub> Activated Carbon *J. Dispers. Sci. Technol.*



37 1671–81.

- [14] Ni X, Li Q, Yang K, Deng H and Xia D 2023. Efficient degradation of Congo red by persulfate activated with different particle sizes of zero-valent copper: performance and mechanism *Environ. Sci. Pollut. Res.* **30** 70054–64.

# *General conclusion*

Activated carbon can be derived from various sources and finds applications in water purification, air filtration, gas adsorption, and medical treatments due to its high porosity and surface area, effectively removing impurities and toxins. This valorization of agricultural waste offers a sustainable solution for environmental and industrial challenges.

Transforming *Ziziphus Lotus* seeds into activated carbon offers a dual benefit: it not only mitigates agricultural waste but also presents a sustainable remedy for environmental and industrial concerns. The seeds of *Ziziphus* are found within the fruit. These seeds are often discarded after the fruit is consumed or processed. However, they have garnered interest due to their potential as a source of activated carbon.

In this context, *Ziziphus Lotus* Seeds were utilized as a precursor for synthesizing activated carbon through chemical activation employing sodium hydroxide (NaOH) as the activation agent. The synthesis process adheres to specific parameters, including an impregnation ratio of 1:1, with stirring for 6 hours, a carbonization temperature of 550°C, a carbonization duration of 1 hour, and a heating rate of 10°C per minute. Additionally, it entails preparing two activated carbons from these seeds using two distinct methods.

For characterization, using SEM images, it was found that a porous structure had formed in the two activated carbons during the activation and carbonization phases, FTIR analysis were evidenced the presence of different functional groups on the surface of the synthesized activated carbons. exhibited a low surface area ( $S_{BET}$ ) of ranging from 37.6432  $m^2/g$  to 9.7211  $m^2/g$  were obtained activated carbons AC1 and AC2 respectively.

The second objective of our study was to optimize the adsorption of the Congo red (CR) dye by the activated carbons we prepared. The CR molecule serves as a model for pollution in aqueous environments. Our aim was to demonstrate how to achieve the highest possible efficiency by implementing a methodology based on experimental design.

## General conclusion

---

The study utilized Matlab software, linking the response variable to various process parameters. Three process parameters,  $x_1$ (initial concentration),  $x_2$  (contact time),  $x_3$  (adsorbent mass). were chosen to evaluate their impacts on the removal efficiency (R%) of CR. The ranges of the factors were selected according to several preliminary experiments. This experimental design was performed as a three-factor consisting of 14 experiments. The results showed that the maximum adsorption capacity of CR on the synthesized AC1 and AC2 were 4 g of adsorbent for 1hour 60% and 3.5 g of adsorbent for 2 hours 70 % respectively.