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ACADEMIC MASTER'S END OF STUDY THESIS

Sector: Process Engineering
Option: Materials Process Engineering

Theme

Modification and characterization of activated carbon-supported metallic nanoparticles

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DEDICATION

With the expression of my gratitude, I dedicate this modest work to those who, whatever the terms embraced, I could never express my sincere love to them.

To the man, my precious offer from the god, who owes my life, my success, and all my respect: my dear father.

To the woman who suffered without letting me suffer, who spared no effort to make me Happy: my adorable mother.

To my beloved sisters and my fiance who has not ceased to advise, encourage and support me throughout my studies. May God protect them and give them luck and happiness.

To my best friend MAROUF Hanane who always knows how to bring joy and happiness to my life.

To my grandparents, uncles and aunts, and cousins. May God gives them a long and happy life.

Thank you for your love and encouragement.

AICI JIHAD

DEDICATION

I would like to dedicate this thesis

To my parents, thank you so much for everything. Words can hardly describe my thanks and appreciation to you. You have been my source of inspiration, support, and guidance. You have taught me to be unique, and determined, to believe in myself. I am truly thankful and honored to have you as my parents.

To my brothers Ilyes and Yacine, who shared with me all the emotional moments during the realization of this work.

I won't forget my best friend AICI Jihad, with whom I spent good and bad times during my university studies.

Finally, I dedicate this work to my dear family, my aunts, uncles, and cousins as a source of hope and motivation, and to everyone who has encouraged me and given me love from near and far.

MAROUF HANANE FATIMA

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ABSTRACT

In this work, we were interested in the modification and characterization of activated carbon-supported by metallic nanoparticles. To clarify more about our experience, it was based on the modification process which is related to the synthesis of two modified activated carbon by metallic nanoparticles, where each of them had different protocols. Secondly, we focused on the characterization methods such as the blue methylene index, the iodine value, and the determination of the point of zero charges, the infrared analysis, and the application of the adsorption on the methylene blue. The experimental results showed that the modified activated carbon that was modified in protocol two was the more efficient one but couldn't exceed the commercial efficiency, going to the application of the activated carbon, the experimental data were analyzed by Langmuir, Freundlich, and Temkin models. it is perfectly described by the Langmuir model with a correlation coefficient of 0.8, The values indicate that our activated carbon produced in the laboratory has a decent affinity for this dye, and the strong adsorption of methylene blue on Merck and modified activated carbon is probably due to the presence of increased porosity.
Keywords: metallic nanoparticles, Activated Carbon, Characterization, Adsorption.

RÉSUMÉ

Dans ce travail, nous nous sommes intéressés à la modification et à la caractérisation du charbon actif supporté par des nanoparticules métalliques. Pour en savoir plus sur notre expérience, celle-ci était basée sur le processus de modification qui est lié à la synthèse de deux charbons actifs modifiés par des nanoparticules métalliques, où chacun d'entre eux avait des protocoles différents. Ensuite, nous nous sommes concentrés sur les méthodes de caractérisation telles que l'indice de méthylène bleu, l'indice d'iode, la détermination du point de charge zéro, l'analyse infrarouge et l'application de l'adsorption sur le bleu de méthylène. Les résultats expérimentaux ont montré que le charbon actif modifié dans le protocole deux était le plus efficace, mais qu'il ne pouvait pas dépasser l'efficacité commerciale, En ce qui concerne l'application du charbon actif, les données expérimentales ont été analysées par les modèles de Langmuir, Freundlich et Temkin. Il est parfaitement décrit par le modèle de Langmuir avec un coefficient de corrélation de 0,8, Les valeurs indiquent que notre charbon actif produit en laboratoire a une affinité décente pour ce colorant, et la forte adsorption du bleu de méthylène sur le charbon actif Merck et le charbon actif modifié est probablement due à la présence d'une porosité accrue.
Mots-clés : nanoparticules métalliques, charbon actif, caractérisation, Adsorption.

ملخص

في هذا العمل، كنا مهتمين بتعديل وتوصيف الكربون المنشط المدعوم بالجسيمات النانوية المعدنية. لتوضيح المزيد عن تجربتنا، فقد استندت إلى عملية التعديل المتعلقة بتأليف اثنين من الكربون المنشط المعدل بواسطة الجسيمات النانوية المعدنية، حيث كان لكل منهما بروتوكولات مختلفة. ثانيًا، ركزنا على طرق التوصيف مثل مؤشر الميثيلين الأزرق، وقيمة اليود، وتحديد نقطة الشحنات الصفرية، وتحليل الأشعة تحت الحمراء، وتطبيق الامتزاز على الميثيلين الأزرق، وأظهرت النتائج التجريبية أن الكربون المنشط الذي تم تعديله في البروتوكول الثاني هو الأكثر كفاءة ولكنه لا يمكن أن يتجاوز الكفاءة التجارية، والذهاب إلى تطبيق الكربون المنشط، تم تحليل البيانات التجريبية بواسطة نماذج Langmuir وFreundlich و. Temkin تم وصفه بشكل مثالي بواسطة نموذج Langmuir مع معامل ارتباط يبلغ 0.8، تشير القيم إلى أن الكربون المنشط الناتج في المختبر لديه تقارب لائق لهذه الصبغة، ومن المحتمل أن يكون الامتصاص القوي للميثيلين الأزرق على Merck والكربون المنشط المعدل ناتجًا عن لوجود مسامية متزايدة.
الكلمات المفتاحية: الجسيمات النانوية المعدنية، الكربون المنشط، التوصيف، الامتزاز.

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General introduction

Nanotechnology is an applied science that focuses on designing, creating, characterization, and applying nanoscale materials and devices. It involves investigating nanoscale phenomena and handling materials, displaying novel properties due to their size and structure. Nanotechnology's unique feature is the increased surface area to volume ratio, presenting new opportunities for surface-based sciences in many nanoscale materials.

Nanoparticles or nanomaterials are particles with sizes ranging from 1 to 100 nanometers, which exhibit unique physical, chemical, and mechanical properties due to their large surface area and quantum effects. They have been used to modify the surface of activated carbon to improve its adsorption properties, selectivity, and reactivity.

Activated carbon is a versatile adsorbent material used in various industrial and environmental applications, mainly due to its high porosity and large surface area. However, the efficiency of activated carbon can be further improved by modifying its surface properties through various methods such as chemical, physical, and biological modifications.

The modification of activated carbon by nanoparticles includes the use of various types of nanoparticles such as metal, metal oxide, carbon-based, and ceramic nanoparticles. These nanoparticles can be coated onto the surface of activated carbon using various techniques such as sol-gel, electrostatic adsorption, and chemical synthesis.

One of the necessary nanomaterials for the environment is the oxide of zinc. Zinc oxide is one of the richest structures that have many advantages. So ZnO has many applications in the different studies of research (Ni and al. 2005; Chen and al. 2007; Salavati-Niasari and al. 2009). Many methods have been used for synthesizing the ZnO such as the soft chemical method (Vay-series 2003), sol-gel process (Zhang et al. 2003), vapor phase growth (Sun and al. 2004), vapor-liquid–solid process (Gao and Wang 2004), electrophoretic deposition (Liu and al. 2003; Illy and al. 2005), thermal evaporation (Umar and Hahn 2006), homogeneous

precipitation (Liu and al. 2007), chemical vapor deposition (Okazaki and al. 2011), chemical bath deposition (Yuliarto and al. 2015), etc. [01].

The characterization of nanoparticle-modified activated carbon includes several techniques such as scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier transform, infrared spectroscopy, and thermogravimetric analysis. These techniques allow the study of the morphology, crystal structure, chemical composition, and thermal stability of the modified activated carbon.

In the present work, zinc oxide nanoparticles (ZnO-NP) were fixed onto AC (Merck) to enhance its sorption capacity.

This thesis consists of three chapters:

In the first chapter, we will briefly present the activated carbons, and see these manufacturing methods and their main characteristics. We will also discuss the effects of nanotechnology on the environment as well as the procedures utilized to create nanoparticles and their applications. Mention one of the necessary nanoparticles which is the oxide of zinc and its characteristics (structural, electronic, optical, chemical, and catalytic properties). Finally, the phenomenon of adsorption is the principal physical reaction involved in the solid-liquid equilibrium without chemical reaction. We explain the different adsorption models that we used in the interpretation of our results.

The second chapter introduces the various characterization techniques, including the iodine index for measuring microporosity, the methylene blue index for measuring mesoporosity, and the Boehm titration, IRTF analysis, and pHPCZ, the chemical characterization of the coal surface is evaluated to determine the functional groups that are present. Attention is also given to the application of methylene blue adsorption of the activated carbon. We'll go also over the procedures and the synthesis of the two given protocols.

The experimental findings and their interpretation are covered in the third and final chapter.

CHAPTER I:

BIBLIOGRAPHIC STUDY

I. Activated carbon:

I.1. Definition:

Activated carbon is an inert porous carbon that has been treated to increase its surface area. It thus has a very large specific surface area that can range from 500 to 2000 m². g⁻¹ hence its high adsorption capacity.

The structure of activated carbon is close to that of graphite, ordered in the form of a stack of flat successive layers of carbon atoms arranged in regular hexagons.

Activated carbon is a non-specific adsorbent with a well-developed porous structure formed, as shown in Figure.01
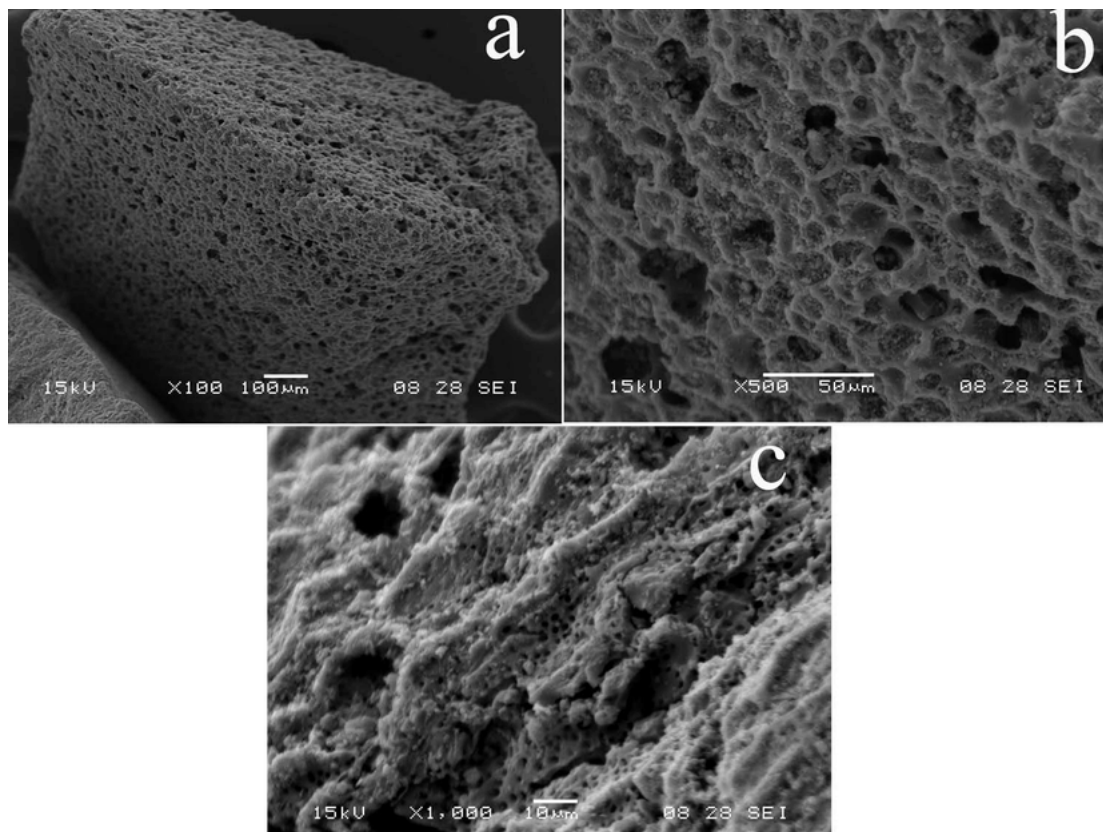
Figure 01. structure of activated carbon seen under an electron microscope.

I.2. Production of activated carbon:

Activated carbon. The diagram below very briefly presents the two major production steps of this adsorbent (Figure.02)

Raw materials

Physical activation

chemical activation

Carbonisation
(600-900 °C, N_2/Ar)

Mixture of precursor and activating agent
(H_3PO_4/KOH/NaOH)

Carbonisation
(450-900°C, N2)

Activation (600-1200°C, CO_2/H_2O)

Washing, drying and grinding

sieving
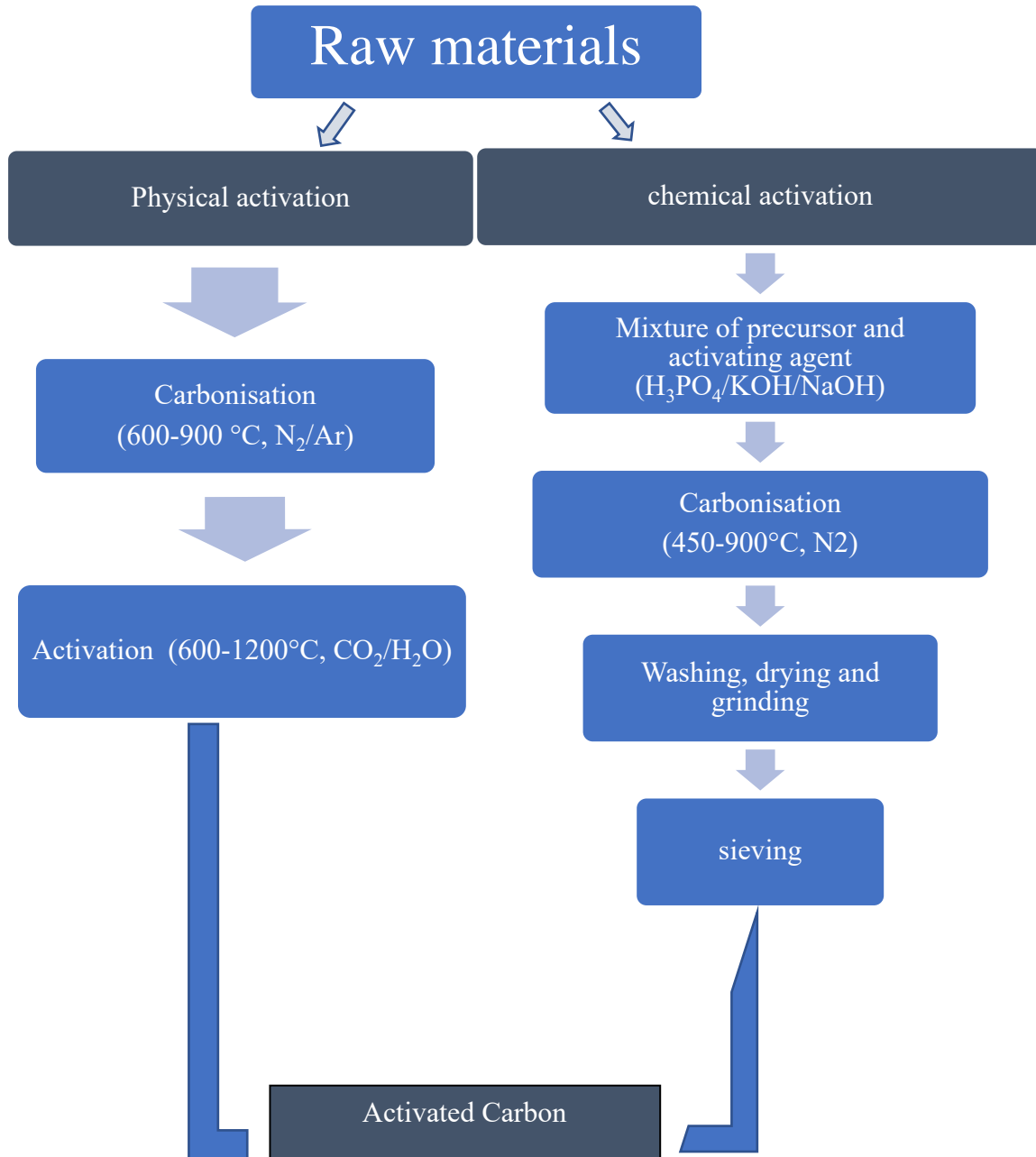
Activated Carbon

Figure 02. schematic process diagram of activated carbon production.

I.2.1. Carbonization:

Agricultural production residues must undergo additional processing to transform the organic matter into graphite. This is done using a "carbonization" step. Carbonization is the thermal decomposition of carbonaceous organic matter under a vacuum or an inert atmosphere in which a sample is subjected to high temperatures between 400 and 800°C to obtain an amorphous carbon-rich solid. The carbonization is generally carried out at a temperature rise rate high enough to minimize contact between the carbonized products and the volatile products. Finally, carbonization is a process during which the starting materials will be modified as follows:

- Enrichment of carbon and loss of volatile compounds; during this stage, the heteroatoms (oxygen and hydrogen) are eliminated and the material becomes richer in carbon.

- Development of internal porosity or space, resulting from the loss of volatiles.

- Gradual cross-association of the carbon-enriched material and in this way create a rigid solid.

The goal of pyrolysis is to obtain a highly carbonaceous "charred" product, with a rudimentary microporosity which can then be developed in the activation process, in this way the char becomes an "activated carbon".

• **Chemical and physicochemical transformations during pyrolysis (thermal decomposition of plant materials:**

Was shown by Tang and Bacon that cellulose, hemicellulose, and lignin undergo thermal decomposition within a well-defined temperature range. With the use of techniques such as absorption spectroscopy, X-ray diffraction (RX), thermogravimetric analysis, the study of the evolution of gases during thermal decomposition as well as the study of physical properties, these authors postulated a mechanism for the conversion of cellulose into carbon. This mechanism consists of four successive steps:

(a), desorption of adsorbed water from 150°C; (b), the loss of structural water from cellulose between 150 and 300°C; (c), chain breaking or depolymerization, and breaking of C-O and C-C bonds between 240 and 400°C; and finally, (d), aromatization from 400°C, which results in

the formation of graphite-type layers. Tang and Bacon simplified the mechanism and still worked with fairly gentle heating rates. However, we can admit that the thermal decomposition of plants is the result of the separate decomposition of each of its components. This process can therefore be followed by three main stages: thermal decomposition of hemicellulose between 200 and 260°C, followed by that of cellulose between 240 and 350°C, and finally the degradation of lignin between 280 and 500°C [02].

I.2.2. Activation:

Simple carbonization does not lead to products with a high adsorption capacity because it gives products with a limited porous structure (specific surface of about 10 m^2 /g). So untreated carbon does not have particularly interesting adsorbent properties. On the other hand, if it undergoes an appropriate treatment, the modifications of the physics and the chemistry of the surface give it new characteristics, the term "activated carbon" then takes on its full meaning.

The porous structure is extended during the activation process, which is the second step and whose goal is to increase the volume of the pores. Activation consists in developing the porous structure by eliminating the tars which obstruct the pores (release of the cavities filled with tar during carbonization) and creating surface functions (generally oxidized) which are at the origin of the interactions between the solid and the adsorbed molecules. The product that will result is a product with a set of parameters at the level of its texture (specific surface and porosity) and also at the level of the functional groups (types of organic functions present on the surface). They are essential in the adsorption process. Activation removes disorganized carbon structures. The internal structure of the compound thus obtained is made up of a random assembly of graphite-type "crystallites" [03]. The space between these units constitutes the microporosity of the activated carbon. Two activation pathways are commonly used:

> **a) Physical activation:** Consists of thermal oxidation of the coal obtained (carbonized) at high temperature (750 to 1000°C) for 24 to 72 hours in the presence of a weakly oxidizing gas such as water vapor, CO_2 [04], the air or mixtures of these gases injected under pressure (controlled oxidation process), which will give rise to the microporosity, makes it possible to develop the existing pores and to create others, increasing in a very significant way its specific surface and its adsorption power.

b) Chemical activation: Carbonization and activation can take place simultaneously, and are carried out at temperatures below 700°C, through the thermal decomposition of the raw material impregnated with activating chemical agents such as H_3PO_4, $ZnCl_2$, and KOH…, these chemical agents catalytically promote dehydration. These activation treatments aim to develop and modulate the porous structure of the carbon and lead to a very strong increase in its specific surface.

I.3. The properties of activated carbon:

I.3.1. Different forms of activated carbon:

Activated carbon is generally available in two forms: powder-activated carbon and granulated activated carbon [05]:

• Powdered activated carbon (PAC):

Powdered activated carbon or PAC takes the form of grains, 95-100% of these particles will pass through a sieve of a given mesh size. For example, the ASTM D5158 standard classifies particles with a diameter less than or equal to 0.177 mm as CAP.

Figure 03. powdered activated carbon.

It is used in combination with a clarification treatment, added continuously with the water to be treated with flocculants. It is recommended to use clarifiers to increase the contact time between carbon and water. The dose of ozone required for inter-oxidation is then reduced. The main consequence is that the number of ozonation by-products decreases.

- Advantages of the PCA:
a- Powdered activated carbon is 2 to 3 times cheaper than granular activated carbon.
b- Additional quantities can be added in the event of accidental or temporary pollution peaks.

c- Adsorption is rapid insofar as a large part of the contact surface is directly available.

- Disadvantages of the PAC:

a- Powdered activated carbon cannot be regenerated when mixed with hydroxide sludge.

b- It is difficult to remove the last traces of impurities without adding a very large quantity of powdered activated carbon.

c- The detection of pollution peaks is problematic and its applicable concentration is limited.

• Granulated Activated Carbon (GAC):

GAC can be either in granular or extruded form and is represented by sizes such as 8x20, 20x40, or 8x30 for liquid phase applications and 4x6, 4x8 or 4x10 for vapor phase applications. For example, a 20x40 coal is made up of particles passing through a standard American No. 20 mesh (0.84 mm) but retained by a No. 40 mesh (0.42 mm) [06].

Figure 04. granulated activated carbon.

Granulated activated carbon is used in different types in the water treatment system for the reduction of residual chlorinated oxidants and very low removal of certain disinfection by-products such as bromates and chlorates and also used to remove turbidity and to dissolve organic compounds, odor, stains, and dyes. Granulated activated carbon treatment is recognized as the most effective process against tastes and odors. This low molecular weight compound promotes extended life. It is used for the removal of organic micropollutants and organic matter in the form of dissolved carbon. It is used in filtration for finishing treatments because it improves many parameters related to natural organic matter (NOM): color, taste, smell, and disinfectant demand. In addition, its use in biological filtration makes it possible to obtain biodegradable organic carbon (BOC) removal efficiencies of up to 80 % at 18 °C, but not exceeding 30 % at 8 °C.

- Advantages of GAC:

a- The life of granulated activated carbon depends on the reduction of organic matter and the smoothing of pesticide points. The choice of the type of activated carbon is also decisive in the efficiency of the elimination.

b- Granulated activated carbon can adsorb some or almost all vapors.

c- It has a high adsorption capacity for organic substances, especially solvents.

d- It retains a large number of chemical substances at the same time.

e- It works well in a wide range of temperatures and humidity.

f- It is inert and can be used safely.

g- It is readily available and inexpensive.

- Disadvantage of the GAC:

a- Limited lifespan.

b- Prefiltration: Dissolved fuels and particulate matter can quickly foul the carbon, requiring pretreatment in most cases.

c- Cost: The need to regularly replace spent carbon makes granulated activated carbon more expensive than stripping for high concentrations of contaminants.

d- Hazardous waste: all the coal must eventually be discarded since it can only be regenerated a certain number of times, or not at all in the case of the adsorption of metals or explosive residues. Depending on the characteristics of spent coal, it may be disposed of as hazardous waste, increasing cost and liability.

I.3.2. AC porous structure:

The pores are classified according to their diameter, in three types of porosity, according to the definition of the IUPAC.

Typical ranges are given in Table 01 but by special procedures, it is possible to prepare activated carbons with even higher porosity, surface area, and adsorptive capacity (ASTTE, 2006): [07]

Table 01. Different types of pores sizes of typically activated carbons (ASTEE, 2006).

	Diameter (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
Macropores	> 50	0.20 - 0.80	0.5 - 2
Mesopores	2 - 50	0.02	20 - 70
Micropores	< 2	0.10	600 -1900

The specific surface depends directly on the porosity: the greater the microporosity, the greater the specific surface. Adsorption on the surface of macropores is often negligible compared to that in micropores and mesopores.

II. Nanotechnology and the Environment:

II.1. Metal Nanoparticles:

Nanotechnology mentions to the subdivision of science and engineering keen to materials. Nanoscience is the study of the phenomena at 1-100 nm particle size and nanomaterials are those which have structured components with at least one dimension less than 100 nm. Nanomaterials derived from nanoparticles Since the past decade nanoparticles have grown as a separate class of materials. Due to the high conductivity of metal nanoparticles, it has received great scientific interest as compared to metal oxide nanoparticles. Metal nanoparticles do not represent a metal-metal chemical bond and are defined as isolated particles between 1-100 nm in size. Metal nanoparticles (NPs) have extraordinarily different properties as compared to their bulk metal which mostly contains a degenerated density of energy states and a large surface-to-volume ratio along with the sizes in the nanometer scale. Therefore, they show high chemical activity and specificity as compared to bulk metals so they are attractive to use as catalysts. The high surface-to-volume ratio along with size effects (quantum effects) gives metal nanoparticles distinctively different properties (chemical, electronic, optical, magnetic, and mechanical) from those of bulk metal. Researchers have achieved considerable attention in nanomaterials because of their unique properties and various applications in

different areas. In the past two decades, nanoparticles exhibit many fascinating applications in a wide variety of fields including conductors, electronics, sensors, photovoltaic devices, drug delivery, catalysis fuel cells, light-emitting diodes, industrial lithography, quantum dots, quantum wires, quantum devices optical and biological devices, etc. Due to their unique properties, which vary from molecular or bulk materials [08]. Incredible properties of nanoparticles intensely depend on the distinct shape and diminutive size of nanoparticles, surrounding media, and their fabrication method. So, scientists take an interest in targeting the fabrication of metal nanoparticles. Different shapes and sizes of metal nanoparticles allow for exploring their applications in fields including catalysis, electronics, sensor, and optical device.

II.2. Uses of Nanotechnology:

Is revolutionizing many technology and industry sectors, such as information technology, homeland security, medicine, transportation, energy, food safety, and environmental science. It can tailor the structures of materials at extremely small scales to achieve specific properties, making them stronger, lighter, more durable, more reactive, more sieve-like, or better electrical conductors. Nanoscale additives to or surface treatments of fabrics can provide lightweight ballistic energy deflection, and clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make. They are water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive. Nanoscale additives in polymer composite materials are being used in baseball bats, tennis rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housings. Carbon nanotube sheets are being produced for use in next-generation air vehicles. Nanoparticles are used in catalysis to boost chemical reactions, saving money and reducing pollutants. Nano-engineered materials make superior household products such as degreasers and stain removers, environmental sensors, air purifiers, filters, antibacterial cleansers, and specialized paints and sealing products.

II.3. Some applications of nanotechnology by type of nanoparticle:

1. **Metal nanoparticles:** They can be used in electronics and optical devices like sensors and displays. They can also be used in drug delivery systems to enhance the effectiveness of drugs and reduce their side effects.

2. **Magnetic nanoparticles:** They can be used in biomedicine for targeted drug delivery, magnetic resonance imaging (MRI), and cancer treatment.

3. **Carbon nanoparticles:** They can be used in electronics, particularly in the manufacturing of semiconductors and batteries. Carbon nanoparticles can also be used in drug delivery systems and as antibacterial agents.

4. **Semiconductor nanoparticles:** Also known as quantum dots, they are used in light-emitting diodes (LEDs), solar cells, and displays.

5. **Polymeric nanoparticles:** They are often used in drug delivery systems, with their size and shape being tailored to optimize drug efficacy and minimize potential negative effects. Overall, nanoparticles have many diverse and exciting applications in fields such as electronics, medicine, and energy.

II.4. Syntheses of nanoparticles:

There are several methods for producing nanoparticles:

1. Chemical methods: Chemical methods involve the use of chemical reactions to produce nanoparticles. For example, a chemical reduction reaction can be used to produce metal nanoparticles.

2. Physical methods: Physical methods involve changing the physical properties of a material to produce nanoparticles. For example, attrition involves the use of milling equipment to create nanoparticles.

3. Biological methods: Biological methods use living organisms to produce nanoparticles. For example, some bacteria are capable of producing nanoparticles.

4. Bottom-up synthesis: This method involves assembling individual atoms or molecules to create nanoparticles.

5. Top-down synthesis: This method involves breaking down larger materials to produce nanoparticles, such as using lithography to carve out small portions of a material.

6. Sol-gel method: Sol-gel method is used to make ceramics and glasses and involves the conversion of a liquid (sol) into a solid (gel).

Nanoparticles can be created by adjusting the concentration of the sol or the processing conditions. There are many other methods for producing nanoparticles, each with its advantages and disadvantages. The choice of method often depends on the desired size, shape, and properties of the nanoparticles that are required for a specific application.

II.5. Activated carbon-metal oxide nanoparticles:

Activated carbon metal oxide nanoparticles (AC-MONPs) are composite materials consisting of activated carbon, metal oxide, and nanoparticles. These materials have received considerable attention recently in various applications, including environmental remediation, catalysis, energy storage, and drug delivery systems. Activated carbon provides a high surface area and porosity, which increase the adsorption and catalytic activity of the composite material. Metal oxides, such as titanium dioxide, aluminum oxide, and zirconium oxide, provide desirable properties such as thermal stability, electronic conductivity, and specific functionalities important for various applications. Nanoparticles such as silver, gold, and iron oxide, can also be introduced to the AC-MONP composite to provide additional characteristics such as antimicrobial activity, plasmonic properties, and magnetic properties. The synergistic combination of activated carbon, metal oxides, and nanoparticles in AC-MONP composites provides unique properties in various applications. For example, in environmental remediation, AC-MONP composites can remove heavy metals, dyes, and organic pollutants from water. In catalysis, they can enhance catalytic activity and selectivity. In energy storage applications, they can increase capacitance, and as drug delivery systems, they provide adsorption selectivity. Overall, AC-MONP composites represent a promising material with a broad range of potential applications. However, further research is needed to optimize their synthesis, structure, and properties for the targeted end-users and applications.

II.6. Nanoparticles of ZnO:

ZnO nanoparticles are a unique semiconductor with a 3.37 eV gap between valence and conduction bands. They have potential applications in electronics, optoelectronics, catalysis, and biomedicine. These nanomaterials exhibit high stability, and surface area-to-volume ratio, and can be easily synthesized in various sizes and shapes. They are used in solar cells, biosensors, displays, catalysis, and drug delivery systems. Further research is needed to understand the toxicology and biocompatibility of ZnO nanoparticles to maximize benefits while minimizing potential hazards.

II.6.1. Properties of ZnO:

a. Structural properties:

Zinc oxide crystallizes in three different crystalline forms: the hexagonal Wurtzite structure (Phase B4), the blende structure (Phase B3), and the Rocksalt structure (Phase B1).

At room temperature and pressure, ZnO crystallizes following a Wurtzite structure with a hexagonal lattice following the space group P63mc [09]. The unit cell parameters are a = 0.32496 nm, c = 0.52042 nm, and = 120°. Each zinc atom is surrounded by four oxygen atoms and vice versa [10].
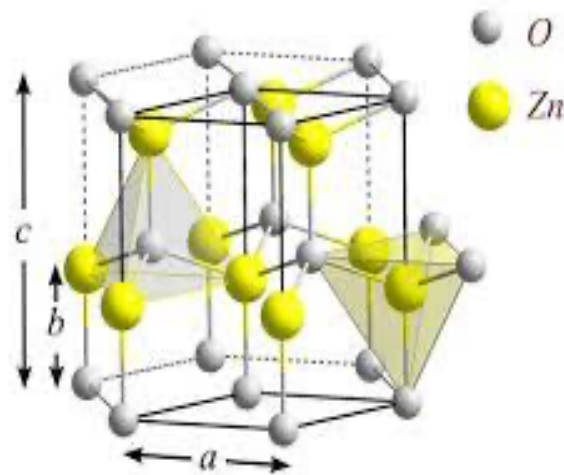
Figure 05. crystallin structure of ZnO (WURTZITE).

b. electronic properties:

We recall that the electronic band structures of oxygen and zinc are: O: $1s^2\ 2s^2\ 2p^4$ Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$. When Zn and O bind in the material they form a semiconductor. The band gap width for ZnO (energy difference between the minimum of the ZnO band conduction and the valence band maximum) is 3.37 eV at room temperature. This value varies with temperature. When foreign atoms are introduced, they can occupy the sites of Zn or O atoms or become interstitial (between two atoms of the network). Similarly, without doping, excess Zn atoms can also move into interstitial positions (ZnO). In the ZnO network, there are also vacant (unoccupied) places of oxygen. These imperfections are called "structural defects". Their energies are always located in the forbidden band. Doping or intrinsic defects play a very important role in the characteristics of the semiconductor. They can considerably modify their properties to obtain materials with adjusted parameters for particular applications by simply modifying the characteristics of the dopant (type, nature, temperature, concentration, doping technique, etc.) [11]. ZnO exhibits a natural n-type electrical conductivity which is due to the presence of interstitial zinc atoms [12].

c. Optical properties and luminescence:

Zinc oxide is a transparent material with a refractive index of 2, and its absorption coefficient varies depending on the conditions of elaboration. Its photoluminescence (PL) spectrum is characterized by the high energy of the first and second exciton, comparable to ambient thermal agitation of 26 meV.

d. Chemical and catalytic properties:

Zinc oxide is a catalyst due to its crystal lattice and semi-conductor properties. It is used as a trap and chemical gas sensor and can act as a photochemical catalyst for reactions such as oxidation of oxygen to ozone, oxidation of ammonia to nitrate, reduction of methylene blue, synthesis of hydrogen peroxide, and oxidation of phenols.

III. General information on the phenomenon of adsorption:

III.1. Definition:

A change in concentration at the interface of two immiscible phases is one of the physical and chemical effects of adsorption. As a result of several more or less intense processes, gas or liquid molecules adhere to the solid surfaces of adsorbents in this phenomenon Figure 06.

The chemical that adsorbs is known as "adsorbate," and the solid that it adsorbs is known as "adsorbing." A substance's ability to bind to the surface of a solid depends mostly on the latter's structural and textural characteristics, particularly the quantity and shape of its pores and the nature of its surface functions. The process by which the adsorbed molecules or atoms separate from the substrate is known as desorption.
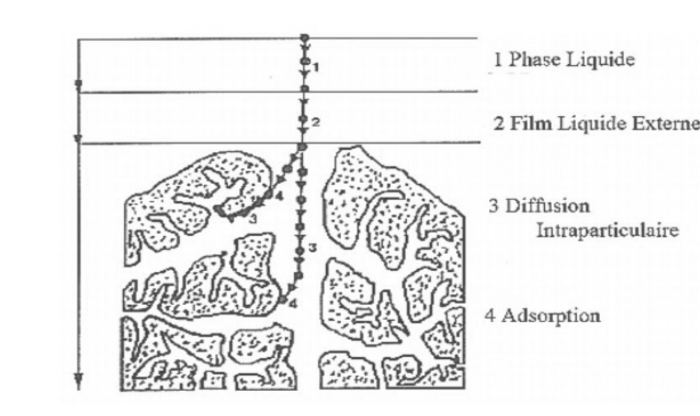

Figure 06. The process of adsorption.

III.2. The different types of adsorptions:

III.2.1. Physical adsorption or physisorption:

Physisorption is a phenomenon in which Van Der Waals forces (an electrostatic bond) are primarily responsible for the adsorbate molecules' adhesion to the adsorbent surface. It takes place without causing any changes to the chemical structure and is completely reversible (the adsorbed molecules can be removed with ease by lowering the pressure or raising the temperature). Physical adsorption is a quick process that includes only weak intermolecular interactions between adjacent particles. Physisorption, in contrast to chemisorption, is an unpredictable event. specific factors causing the development of multilayers: The first layer results from adsorbate/adsorbent interactions, whereas the subsequent layers are related to adsorbate/adsorbate interactions.

III.2.2. Chemical adsorption or chemisorption:

It comes about as a result of a chemical reaction between the adsorbent molecules that make up the surface. both solid and liquid molecules. These chemically-based attraction forces result in an electron transfer or pooling, which destroys the individuality of the molecules and the development of a chemical compound on the adsorbent's surface. This adsorption guy forms at high temperatures and activates a high energy of transformation.

III.3. Adsorption mechanism:

Adsorption results globally in the reduction of the concentration of one or more liquid phase elements; it is also the result of the succession of several stages of intermediaries. For the adsorbate to complete its journey fixed to an adsorbent site, it must have passed at least four stages listed as follows:

1. Adsorbate diffusion from the exterior liquid phase to the region around the adsorbent surface.
2. Diffusion of materials outside of grains (transfer of solute through the liquid film to grain surface).
3. Intragranular matter transfer is the movement of the material inside the porous structure of the seeds from their outer surface to the active areas.
4. Once the adsorption reaction comes into contact with the active sites, the molecule is regarded as stationary.

III.4. Adsorption Models:

III.4.1. The Freundlich model:

Freundlich isotherm applies to adsorption processes that occur on heterogonous surfaces [15]. This isotherm gives an expression That defines the surface heterogeneity and the exponential distribution of active sites and their energies.

The linear form of the Freundlich isotherm is as follows [13]:

$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_{e'} \ .... \ (1)$$

where qe is the equilibrium sorption concentration of solute per gram of adsorbent (mg g^{-1}); Ce is the equilibrium aqueous concentration of the solute (m g L^{-1}); K_f and n are Freundlich constants which are related to the adsorption capacity and the intensity of adsorption. A value of n between 2 and 10 shows good adsorption [14].

III.4.2. The Langmuir model:

Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents [15]. Langmuir isotherm accounts for surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [16].

The Langmuir equation can be written in the following linear form [17]:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_e} + \frac{C_e}{q_m} \ .... \ (2)$$

where q $_m$ and K $_L$ represented the maximum adsorption capacity and the Langmuir constant, respectively. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L defined as (3) [18]:

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

where C_0 is the initial concentration. R_L values indicate the adsorption to be unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, and irreversible when $R_L = 0$.

II.4.3. The Temkin model:

This isotherm contains a factor that explicitly takes into account adsorbent-adsorbate interactions. The Temkin isotherm can be expressed by the following equation 4 [19]:

$$q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_{e'} \quad \ldots\ldots\ldots \quad (4)$$

where R T/b= b (J mol $^{-1}$), which is the Temkin c constant related to the heat of sorption whereas A (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.31 4 J mol $^{-1}$ K^{-1}) is the universal gas constant and T (K) is the absolute solution temperature.

CHAPTER II:

EXPERIMENTAL STUDY

II.1. Preparation of Nanocomposite AC-ZnO:

1. AC-Merck:

Merck is a well-known company that produces a wide range of chemicals and laboratory equipment. While Merck does not manufacture activated carbon, they do sell powdered activated carbon that can be used for various laboratory applications. Merck offers a range of activated charcoal powders that vary in purity, particle size, and other characteristics. Some examples of activated charcoal powders sold by Merck are:

- Powdered activated carbon, Norit (R) USP, for medicinal and analytical applications.
- Powdered activated carbon, analytical grade, suitable for research and development purposes.
- Powdered activated carbon, decolorizing, for use in analytical and research applications.
- Powdered activated carbon, high activity, for decolorization and purification applications.

It is important to note that, as with any chemical or laboratory reagent, appropriate safety measures must be taken to handle Powdered activated carbon. Always follow the manufacturer's instructions and appropriate safety protocols when using and storing Powdered activated carbon, and consult with a trained professional if you are not familiar with the proper handling and use of this material.

2. Procedure 1 (P1):

- A solution of ammonium carbonate $(NH_4)_2CO_3$ was added vigorously with 10g of AC (Merck) and Zinc sulfate-7-hydrate $(ZnSO_4-7-H_2O)$ solution was combined drop by drop to the mixture, we noticed that a white precipitate was formed on the activated carbon;
- The nanoparticles began to form immediately within 2 min like a white colloidal precipitate turning grey as a result of a homogeneous mixture with black;
- The reaction was allowed to age for 3 hours which grey particles of paste is formed;
- We filter the loaded ZnO-AC using a Whatman filter paper;
- We dry the rinsed nanocomposite in a hot air oven at 105 °C for One night and then calcined it in a furnace for 4 hours at 550 °C;

- We rinse the nanocomposite three times with lukewarm water until the pH was neutral and we let it dry in a hot air oven;

- We cool the composite and store it in an airtight container.

3. **Procedure 2 (P2):**

- We combine 100 ml of Zinc sulfate-7-hydrate ($ZnSO_4$-7-H_2O) and 100 ml of Carbonate ammonium $(NH_4)_2CO_3$ in a beaker, and a white precipitate was formed;

- After that, we add 10 g of AC-Merck;

- The reaction was agitated for 3 hours;

- We filter the loaded ZnO-AC using a Whatman filter paper and let it age for one night;

- We dry the nanocomposite in a hot air oven at 105°C for one night and then calcined it in the furnace for 4h at 700 °C;

- We rinse the calcined nanocomposite repeatedly three times with lukewarm water;

- We let it anhydrous in a hot air oven for one night.

II.2. Preparation of the adsorbent:

The material was washed with refined water and oven-dried for one night with a loss of mass (for P1 is almost 3 grams, and for P2 is 4 g). At that point, all the AC is ground and sieved to get a last grain estimate of 50 µm.

II.3. Characterization methods:

The fitting characterization strategies are:

- The assurance of the iodine number for microporosity.

- The assurance of the methylene blue index for mesoporosity.

- The IR strategy for functional groups.

- Boehm's method for the assurance of acid-base groups on the surface of activated carbon.

- The pH of Zero of point Charge (pH_{zpc}).

II.3.1. Iodine number:

II.3.1.1. Definition:

The iodine number gives a sign of the microporosity of the carbon. Usually, the number of milligrams of iodine adsorbed per gram of adsorbent at a leftover concentration of 0.02 N [20].

II.3.1.2 Iodometric method:

Iodometry concerns the response with a standard arrangement of iodine. It is related to iodine titration discharged in chemical responses:

$$I_2 + 2\ e^- \longrightarrow 2\ I^-$$
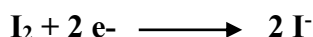
Examination by iodometry is based on oxidation-reduction marvels, on the off chance that free iodine is included in an arrangement of sodium thiosulfate (reducer), the taking-after response happens (25):

$$2\ S_2O_3{}^{2-} + I_2 \longrightarrow 2\ I^- + S_4O_6{}^{2-}$$

II.3.1.3. Preparation of solutions:

➢ To prepare a standard Iodine Solution (I_2) 0.1N, Weigh 12,69g of iodine and 27g of potassium iodide (KI) into a beaker. Mix the dry iodine (I_2) and potassium iodide (KIO_3). Add 2 to 5 mL of water to the beaker and stir well. Continue adding small increments of water (approximately 5 mL each) while stirring until the total volume is 50 to 60 mL. Allow the solution to stand one night to ensure that all crystals are thoroughly dissolved. Occasional stirring during this period will aid in the dissolution. Quantitatively transfer to a 1L volumetric flask and fill to the mark with distilled water. Store the solution in an amber bottle.

➢ To prepare a Sodium Thiosulfate solution ($Na_2S_2O_3$) of 0.1N Dissolve 24.82g sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in approximately 75mL of freshly boiled distilled water. Quantitatively transfer the mixture to a 1L volumetric flask and dilute to the mark. The solution should be stored in an amber bottle.

➢ To prepare an arrangement of Hydrochloric Acid (HCl) Solution (5 % v/v) we Add 10 ml of concentrated hydrochloric acid (HCl) in a flask of 200 ml and mix well.

II.3.1.4. Procedure:

To determine the iodine number of each activated carbon, it is necessary to prepare:

1- A solution of hydrochloric acid with a concentration of 5% (v/v).
2- A 0.1 N iodine solution.
3- A solution of sodium thiosulfate with a concentration of 0.1 N.

Weigh 0.2g of the sample which has been previously dried at 150°C in the oven for 3 hours, transfer it to a flask, add 10 mL of HCl, and stir gently until the sample is completely wet, boil it for 30 seconds, allow it to cool to the room temperature, transpose 100 mL of the iodine solution into the flask, cap it immediately and shake vigorously for 30 seconds, filter, then discard the 20 to 30 mL of the filtrate and collect the rest in a beaker.

Pipette 50 cm3 of the filtrate into a clean 250 mL Erlenmeyer flask, titrate with $Na_2S_2O_3$ until the solution becomes transparent, note the volume V', and finally, calculate the molarity of the filtrate R from the following equation:

$$R = \frac{0,001 * V'}{2} \ldots\ldots\ldots(5)$$

Calculate the correction factor (D) which is given by the following relation:

$$D = \left(\frac{0,01}{R}\right)^{0.165} \ \ldots\ldots (6)$$

Calculate the iodine value using the following relationship:

$$Iodine\ value = \frac{[1269,3 - (V' * 27,92)] * D]}{m} \ldots\ldots\ldots(7)$$

Where: R: the molarity of the filtrate.

D: the correction factor.

V: the volume of sodium thiosulfate (ml).

m: the mass of activated carbon (g).

II.3.2. Determination of the methylene blue value and Accessible surface:

- **Methylene Blue value:**

II.3.2.1. Definition:

The methylene blue value indicates the adsorption capacity of activated carbon for molecules having similar dimensions to methylene blue. It is a quick method for comparing different batches of activated carbon of the same quality.

II.3.2.2. Principle:

The methylene blue value is defined as the number of milliliters of standard methylene blue solution decolorized by 0.1 g of activated carbon [21].

II.3.2.3. Preparation of solutions:

To arrange a solution of acetic acid (CH_3COOH) (0.25%). Take 2.5mL of fuming acetic acid in 900ml of distilled water in a 1L flask and dilute to the mark.

To concoct a solution of acetic acid (CH_3COOH) (50%), take 253.11ml of fuming acetic acid in a vial and dilute to the mark.

To prepare a concentration MB solution (1200mg), weigh 1.2g of BM and dissolve in 100mL of acetic acid (50%) and dilute to the mark (1L).

From this MB solution, an intermediate solution of 120mg / L (100mL) is prepared,

And diluted with the acetic acid solution (0.25%).

II.3.2.4. Procedure:

To determine the MB value of each activated carbon (Merck, P1, P2), it is necessary to prepare:

1- Solution of acetic acid (0.25%).

2- Solution of acetic acid (50%).

3- Concentration MB solution (1200 mg /L).

4- Pipette different concentrations of MB solution (120 mg/L), put them in 100 mL vials, and dilute with acetic acid (0.25%) up to the mark (1L).

To determine the MB value, weigh 0.1 g of each activated carbon and introduce 25 ml of MB solution with a concentration of 1200 mg /L, then stir for 30 min for each carbon.

Calculate the MB index by the following relationship:

$$\textit{Indices MB (mg/g)} = \frac{(1200 - Ceq)*V}{m*1000} \ldots\ldots \textit{(8)}$$

Where: m: mass of AC (g).

    V: volume of solution (ml).

- **Accessible surface:**

The estimation of the specific surface of an adsorbent is conventionally based on measurements of the adsorption capacity of this adsorbent for a given solute, the molecule of this solute must have an accessible surface.

In a series of beakers, 0.05 g of commercial activated carbon (Merck) is successively introduced and AC-ZnO (P1), AC-ZnO (P2) which is brought into contact with 25 mL of the methylene blue solution of initial concentration C_0, the whole is stirred for a contact time of 2 hours at a temperature of 25 C°. Then the filtrate is analyzed, and the quantity x/m (mass adsorbed per gram of adsorbent) is determined by the equation next:

$$x/m = \frac{(C_0 - Ceq) \times V}{m \times 1000} \ldots\ldots\ldots \textit{(9)}$$

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

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

    m: mass of adsorbent (g).

    V: volume of adsorbate (mL).

    1000: conversion factor.

It suffices for this purpose to determine the value of the adsorption capacity of the monolayer from the adsorption isotherm (Langmuir model).

For determining the surfaces accessible to methylene blue in (m^2/g), we use Langmuir's model equation in the linear form:

$$\frac{ceq}{\left(\frac{x}{m}\right)} = \frac{1}{k_L * b} + \frac{1}{b} * c_{eq} \ldots\ldots\ldots\ (10)$$

We can then deduce respectively b from the slope and the ordinate at the origin of the curves $\frac{c_{eq}}{\left(\frac{x}{m}\right)} = f(c_{eq})$. The knowledge of b leads to the determination of the surface S by the relation:

$$S_{BM} = \frac{b \, N \, S}{M_m} \ \ldots\ldots\ldots\ (11)$$

where: b: the maximum adsorption capacity for a monolayer in mg of solute adsorbed per gram of adsorbent, determined by Langmuir.

$N = 6.023 \times 10^{23}$ mol^{-1} (Avogadro's number).

$S = 119\text{Å}^2$ area occupied by a molecule of methylene blue.

M_m: molecular mass of methylene blue (319.86 g/mol).

II.3.3. Boehm titration:

II.3.3.1. Definition:

The determination of acid-base groups on the surface of activated carbon can be made using Boehm's method.

The oxygenated functional groups present on the surface of activated carbon are of different acidity which could be evaluated by titration with strong basic solutions different. A base of a certain strength only neutralizes acids with pKa higher or equal to that of the base [22]. The bases used in the Boehm method are the sodium bicarbonate, $NaHCO_3$ (pKa = 6.37); sodium carbonate, Na_2CO_3 (pKa = 10.25); sodium hydroxide, NaOH (pKa=15.74); and sodium ethoxide, $NaOC_2H_5$ (pKa = 20.58) [23]. The bicarbonate is supposed to neutralize only the carboxylic groups, the sodium carbonate; carboxylic groups and lactones, and sodium hydroxide; the groups phenolics in addition to the last two and finally sodium ethoxide is supposed to react with all oxygenated species (pKa < 20.58 extremely weak acid).

II.3.3.2. Procedure:

A 0.3 mass of commercial activated carbon, AC-ZnO (P1), and AC-ZnO (P2) are put in a vial contact with 30ml of each base of 0.1 N added stirring is maintained t = 48 hours after filtration. The amount of base consumed is determined by titrating a known volume of 10ml filtrate with HCl 0.1 N by adding a color indicator of each base

$$Quantity_{base\ neutralised}\left(\frac{\mathbf{meq}}{\mathbf{g}}\right) = \frac{[N_{base} - (N_{HCL}.V_{HCL}(\mathbf{mL})/V\text{dosed base})].V_{base}}{m_{sample}\,(g)} \dots\dots (12)$$

With: N $_{base}$ = 0.1 N.

N $_{HCl}$ = 0.1 N.

V $_{HCl}$ = V$_{titrated}$ in mL.

V $_{dosed\ base}$ = 10 mL.

V $_{base}$ = 30 mL.

M $_{sample}$ = 0.3 g.

The concentrations of each of the oxygenated groups are calculated according to:

GI= N [NaHCO $_3$] (carboxylic groups)

GII= N [Na $_2$ CO $_3$]- N [NaHCO $_3$] (lactone groups)

GIII= N[NaOH]- N [Na $_2$CO $_3$] (phenol groups)

GIV= N [NaOC $_2$ H $_5$]- N[NaOH] (carbonyl groups)

II.3.4. Determination of point of zero charge pH (pH$_{PZC}$):

II.3.4.1. Definition:

The point of zero charges (pzc) is the pH at which the surface of a material has no net electric charge. At this point, the surface has an equal number of positive and negative charges, resulting in no overall charge. This is important in many fields such as chemistry, electrochemistry, and surface science as it affects the behavior of the material in various environments and the interactions with other substances.

II.3.4.2. Procedure:

0.15 g of each activated carbon was added to 50 ml of 0.01 M NaCl solution of pH ranging from 2 to 12, pH adjusted by the addition of 0.01 M HCl or NaOH solution, were kept

in constant stirring at room temperature for 48 hours and the final pH was measured. The pH_{ZPC} is the point where the pH_{final} = f (initial pH) curve intercepts the first pH_{final} bisector = f (initial pH).

II.3.5. FTIR analyse:

II.3.5.1. Definition:

Solid phase IR absorption spectra were recorded with an FT-IR SPECTROMETER where the studied frequency ranged from 4000 to 400 cm^{-1}, allowing us to characterize the functional groups of interest.

Infrared analysis helps determine the main chemical functions present on the surface of activated carbons.

II.4. Adsorption test on methylene blue:

In this part, we study the isothermal adsorption of methylene blue on activated carbon ZnO-AC (P1) and commercial activated carbon (Merck).

In a series of beakers, a mass of 0.05 g of activated carbon is successively introduced which is brought into contact with 25 mL of the solution of known initial concentration, the whole is stirred for 2h at 25 C°. Then the filtrate is analyzed at λ=665 nm and the quantity x/m (mg/g) is calculated according to equation 09.

The adsorption isotherms are modeled as appropriate, by the classic Langmuir and Freundlich models with satisfactory statistical quality, the acceptable correlation coefficients generally being greater than 0.90. We will be particularly interested in the adsorption isotherms of this pollutant by the activated carbon that we have modified.

CHAPTER III:

RESULTS AND DISCUSSION

III.1. AC-ZnO mass loss:

Table 02. Loss of mass of modified activated carbon (AC-ZnO).

Material	Initial mass	Final mass	loss of mass
AC-ZnO (protocol 1)	12.139	9.198	2.941
AC-ZnO (protocol 2)	13.248	9.243	4.005

The modified activated carbon with ZnO nanoparticles (AC-ZnO) was calcined for 4 hours at a high temperature (550 C°, 700 C°).

When the activated carbon modified by nanoparticles ZnO is calcined, it will undergo a series of thermal decomposition and oxidation reactions that can result in mass loss. Calcination is a process where a material is heated to high temperatures, to drive off the humidity, oxidant agents that came from the modification protocol transform the material into a more stable form. The appearance of mass loss it can be made also by weighing errors.

III.2. Specific surface area:

III.2.1. Iodine number:

The iodine number is a very important parameter in the characterization of activated carbon. To compare commercial activated carbon with two other types of activated carbon obtained, we measured this number for these adsorbents and grouped them into Table 03. And figure 07 represents them in a bar chart.

Table 03. iodine number of the various activated carbons studied.

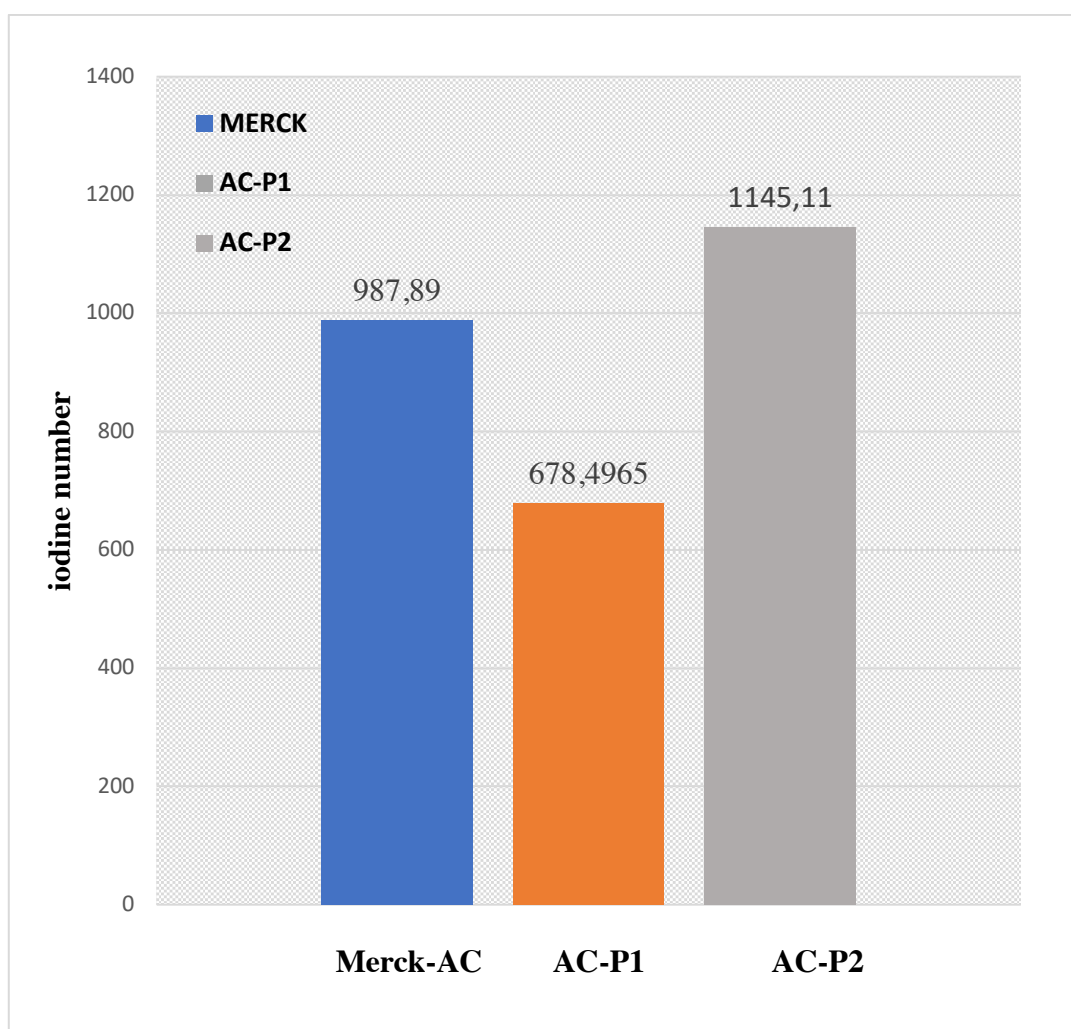| Adsorbents	Activated carbon Merck	AC-ZnO Protocol 1	AC-ZnO Protocol 2
Volumes of (Na$_2$S$_2$O$_3$) (mL)	37.6	40	36.4
Iodine number (mg/g)	987.89	678.496	1145.11

Figure 07. iodine number of the various activated carbons studied.

The results show that the AC-ZnO prepared material of the 2nd protocol has the highest iodine value, followed by the AC-Merck. This value obtained shows that the protocol applied to modified activated carbon in the 2nd protocol produces a material with well-developed microporosity.

So, from the iodine number values, we can say that AC-ZnO has a higher porosity than commercial activated carbon, which is a pleasant value since a good activated carbon should have an iodine value > 900 mg/g.

The literature has shown that activated carbons with an iodine value greater than 950 mg/g are mainly used to measure micropores (0-20 Å) [24].

The adsorbent with the highest iodine number will have the largest specific surface area, with this we can say that it's the AC-ZnO of protocol 2 that this rule applies to.

An iodine number of 1145.11 mg/g for activated carbon modified with ZnO nanoparticles. This value indicates a carbon structure with a microporous tendency [25]. The prepared activated carbon would therefore have a microporous structure.

In the literature many other adsorbents have their iodine value like commercial activated carbon (200,36 mg/g), raw moringa leaves, acid, and base activated moringa leaves are 182,29 et 169,18 mg/g respectively [26], and activated carbon based on crushed pine 483,5 mg/g [27].

III.2.2. Boehm titration:

As mentioned in the experimental section, Boehm gives information on the concentration and type of functional groups of commercial activated carbon Merck and AC-ZnO-NC (protocol 1,2). As shown in Table 05.

Table 04. Results of the Boehm test of the three activated carbon studies.

	Merck-AC	ZnO-AC (P1)	ZnO-AC (P2)	Merck-AC	ZnO-AC (P1)	ZnO-AC (P2)
	V_{HCl} (ml)			Quantity of oxygenated groups (meq/g)		
NaOH	8.3	3.9	3.58	1.7	2.2	2.84
Na$_2$CO$_3$	9	4.4	4.57	1	1.2	0.86
NaHCO$_3$	9.5	4.8	4.58	0.5	0.4	0.84
HCl	9.7	4.8	4.8	0.3	0.4	0.4

Table 05. Oxygen-containing functional groups.

	Carboxylic	Lactone	Phenol	Total acidic groups	Total basic groups
MERCK-AC	0.5	0.5	0.7	1.7	0.3
ZnO-AC (P1)	0.4	0.8	1	2.2	0.4
ZnO-AC (P2)	0.84	0.02	1.98	2.84	0.4

The acidic groups of the commercial activated carbon cumulate to a total of 1.7 meq/g, while the basic group is 0.3 mmol/g. basic groups have less significant numbers in comparison to acidic groups suggesting that there are more oxygen-bearing functional groups as depicted in Table 04 hence more acidic sites. Resulted in Nethaji and al. (2013) [28] and Bello and al. (2014) [29].

Moving ahead, the acidic groups of the AC-ZnO of protocol 1 cumulated to a total of 2.2 and 2.82 meq/g for protocol 2, and the total basic groups for both activated carbons is 0.4 meq/g.

As expected, the total amount of surface acidic groups of the modified activated carbon increased after modification contrary to the commercial activated carbon.

These results are confirmed by pHzpc and FTIR analyses of activated carbon studied.
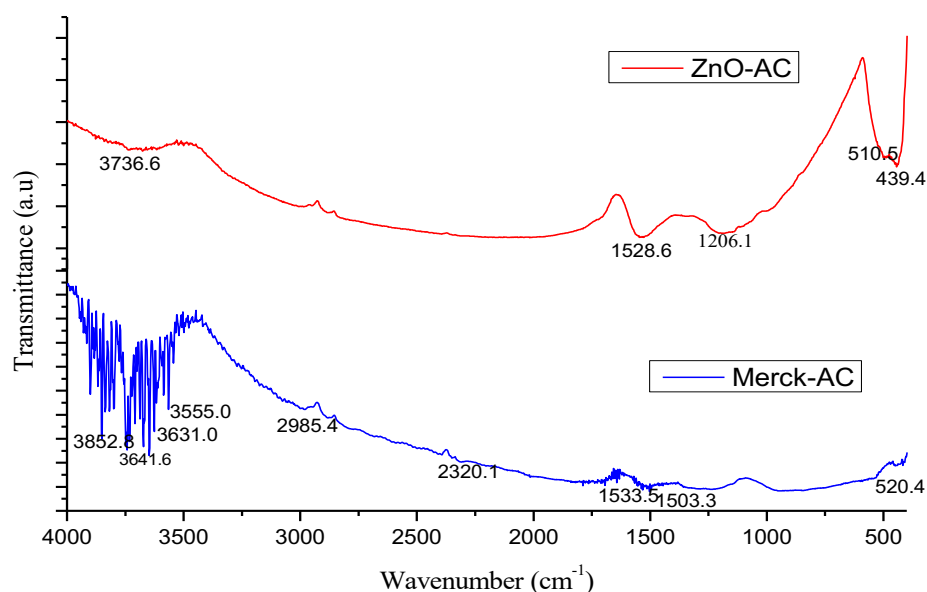
II.2.3. FTIR analyse:

Figure 08. Activated Carbons FTIR Spectrum.

- **For Merck-AC:**

1503.3 cm^{-1}: a weak band may indicate aromatic C=C groups.

1533.5 cm^{-1}: variable aromatic C=C elongation vibration, the presence of C-N=O groups;

2985.9 cm^{-1}: band can be attributed to the stretching of C-H groups.

3555 cm^{-1} to 3852.8 cm^{-1}: these bands can be attributed to the elongation vibrations of the O-H groups in the alcohols or possibly the phenols.

- **For ZnO-AC carbon:**

1206.1 cm^{-1}: a band indicates the presence of alcohol groups, tetrahedral carbon, elongation of ester groups, or anhydride groups.

1528.6 cm^{-1}: a band indicates the elongation of conjugated N-O (NO$_2$) groups or perhaps elongation of aromatic C=C groups.

3736.6 cm^{-1}: this band can be attributed to the stretching vibrations of the O-H groups in the alcohols or possibly the phenols.

III.2.4. Zero Point Charge pH:

The pHpzc is a good indicator of the chemical and electronic properties of the groups. The pHpzc corresponds to the point of intersection of the curve with the straight-line equation pH$_{final}$=pH$_{initial}$.

The adsorption process is known to exhibit a dependency on the pH of the system, as evidenced by variations in its behavior as a function of the pH value. More specifically, the adsorption process is observed to be influenced by the pH at the point of zero charges (pHzpc).

In alkaline solutions, there exists a positive correlation between the pHzpc and the adsorption rate, where an increase in the former leads to a subsequent increase in the latter. Lower pHzpc (potential of the hydrogen ion concentration zone) is directly correlated with acidic solutions.

The adsorption rate is increased to a higher degree. The findings garnered in this study have been delineated in Table 06, accompanied by a corresponding visual depiction portrayed in Figure 09 and Figure 10.

Table 06. Point of zero charges for three adsorbents.

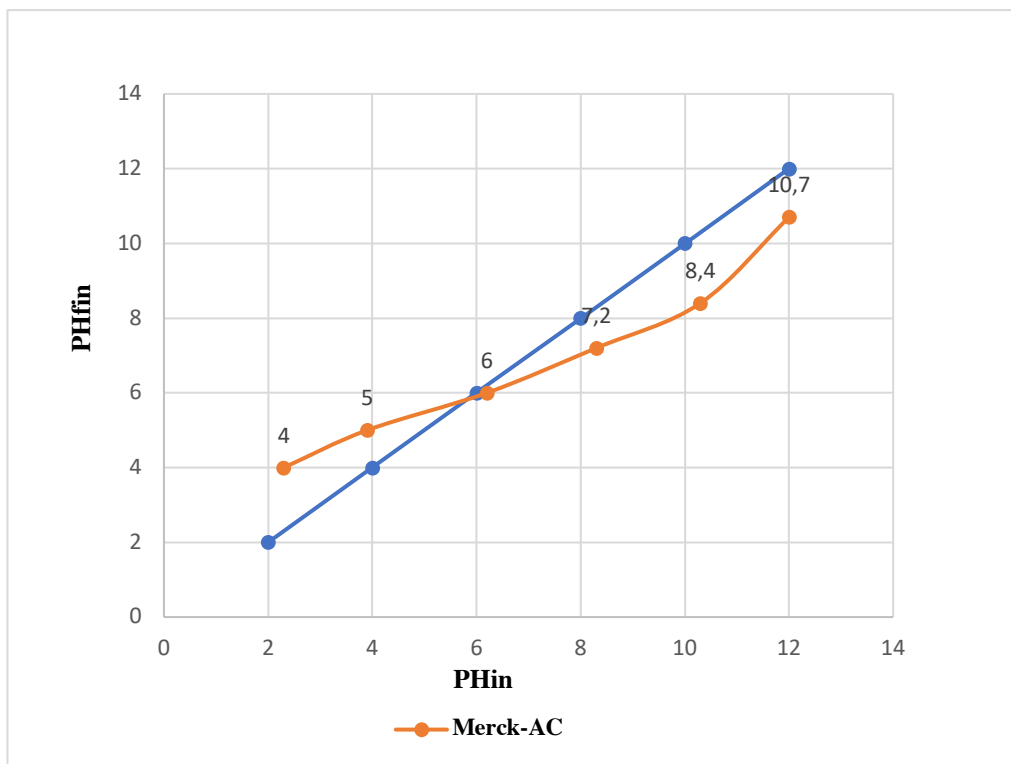| Adsorbent	pH$_{ZPC}$
Merck AC	6.2
AC-ZnO (P1)	8.2
AC-ZnO (P2)	7.6

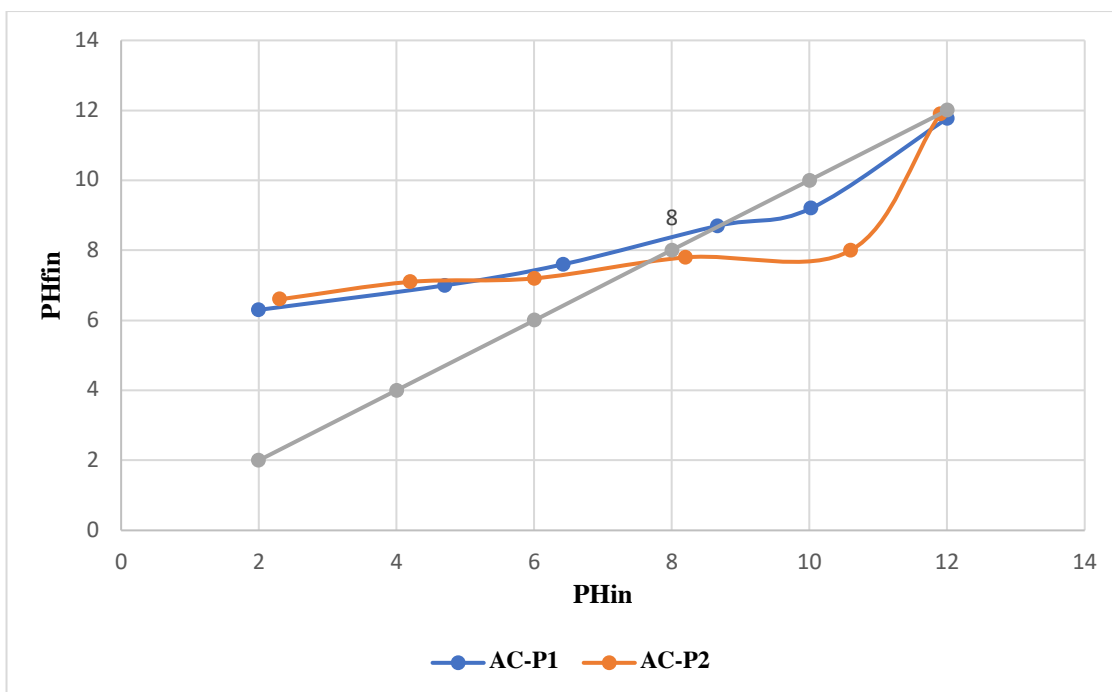**Figure 09**. graphical representation of Merck pH $_{ZPC}$.

Figure 10. Graphical representation of P1 and P2.

Table 06 demonstrates that the Merck-AC pH$_{ZPC}$ (=6.2) dramatically dropped in contrast to the pH$_{ZPC}$ modified one (P1=8.2, P2= 7.6).

Overall, the pH of zero-point charge (pHzpc) is the pH at which the surface charge of an activated carbon particle is neutral, meaning that there are equal numbers of positive and negative surface charges. When the pH of a solution is above the pHzpc of a surface, the surface becomes negatively charged, and when it is below the pHzpc, the surface becomes positively charged. If the pHzpc of all the modified and non-modified AC is lower than the pH of the aqueous solution, it means that they have a more acidic surface. This could be due to the presence of acidic functional groups on the surface of the activated carbons.

The lower pHzpc may affect the activated carbon's surface charge and adsorption properties and may make it more favorable for adsorbing cations than anions.

III.2.5. Bleu Methylene value:

The Bleu Methylene Value is a measure used for characterizing the adsorption capacity of commercial activated carbon with other two modified ones with nanoparticles. It refers to the amount of blue dye (methylene blue) that a specific amount of activated carbon can adsorb from an aqueous solution under certain conditions. It is expressed in milligrams of methylene blue per gram of activated carbon. The higher the Bleu Methylene Value, the more adsorbent the activated carbon is.

Table 07. The values of the methylene blue index of the three activated carbons.

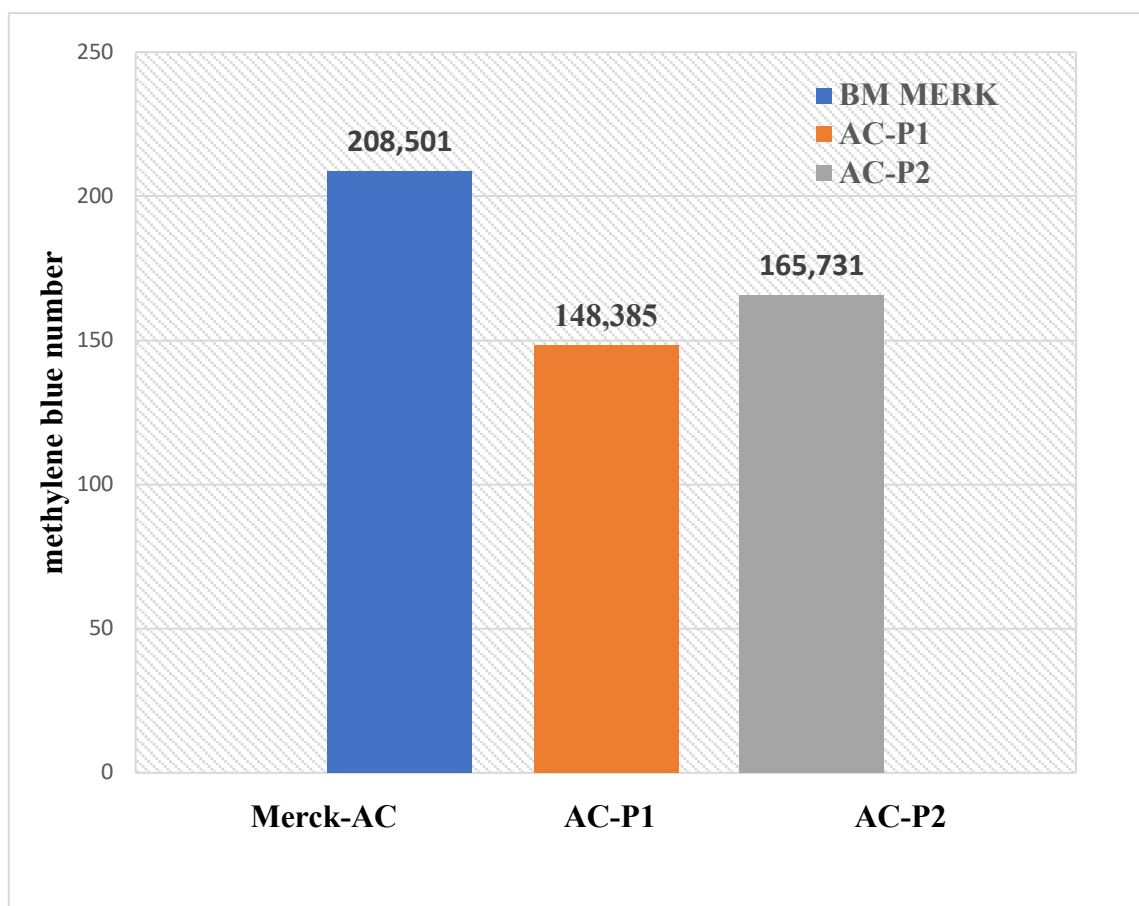| Adsorbents	Activated carbon Merck	AC-ZnO (P1)	AC-ZnO (P2)
C$_0$ (mg/L)	1200	1200	1200
Abs	0.515	1.252	1.014
Diluted factor	50	50	50
C$_{eq}$ (mg/L)	272.77	606.46	590.04
Methylene blue number (mg/g)	208.501	148.384	165.730

Figure 11. Blue methylene value of the various activated carbons studied.

The bar chart provides information about the values of the various activated carbons studied (Activated carbon Merck, AC-ZnO P1, and P2).

Overall, the values that we obtained show that the protocol applied to virgin activated carbon produces a material with well-developed porosity.

And also, we illustrate that from the blue methylene values, we can say that from the two modified protocols, AC-ZnO of protocol 2 has a higher mesoporosity, that is referring to the use of ammonium carbonate as it helps to increase the adsorption of methylene blue by activated carbon as it is a pore-forming agent [30] which caused the formation of additional pores in the activated carbon.

The creation of these additional pores increases the surface area and porosity of the AC which in turn, enhances the adsorption capacity.

Moreover, the highest adsorption capacity of activated carbon, the largest specific

surface area, and the steady growth in the protocol 2 results show that it is the well-used modified activated carbon one.

III.2.6. Adsorption test on methylene blue:

Blue methylene is usually used to characterize the mesoporosity of activated carbons. in our lab experience, we brought a series of beakers, then 0.05 g of Merck activated carbon, and a modified one were successively introduced to them, which brought into contact with 25 mL of the methylene blue solution with an initial concentration of C_0, the whole is stirred for a contact time of 2 hours. Then the filtrate is analyzed at λ=665 nm and the quantity qe (mg/g) is calculated.

Figure 12 shows the adsorption isotherms of methylene blue by the two activated carbons. The figure demonstrates the largest adsorption capacity by Merck and protocol 2 activated carbon.
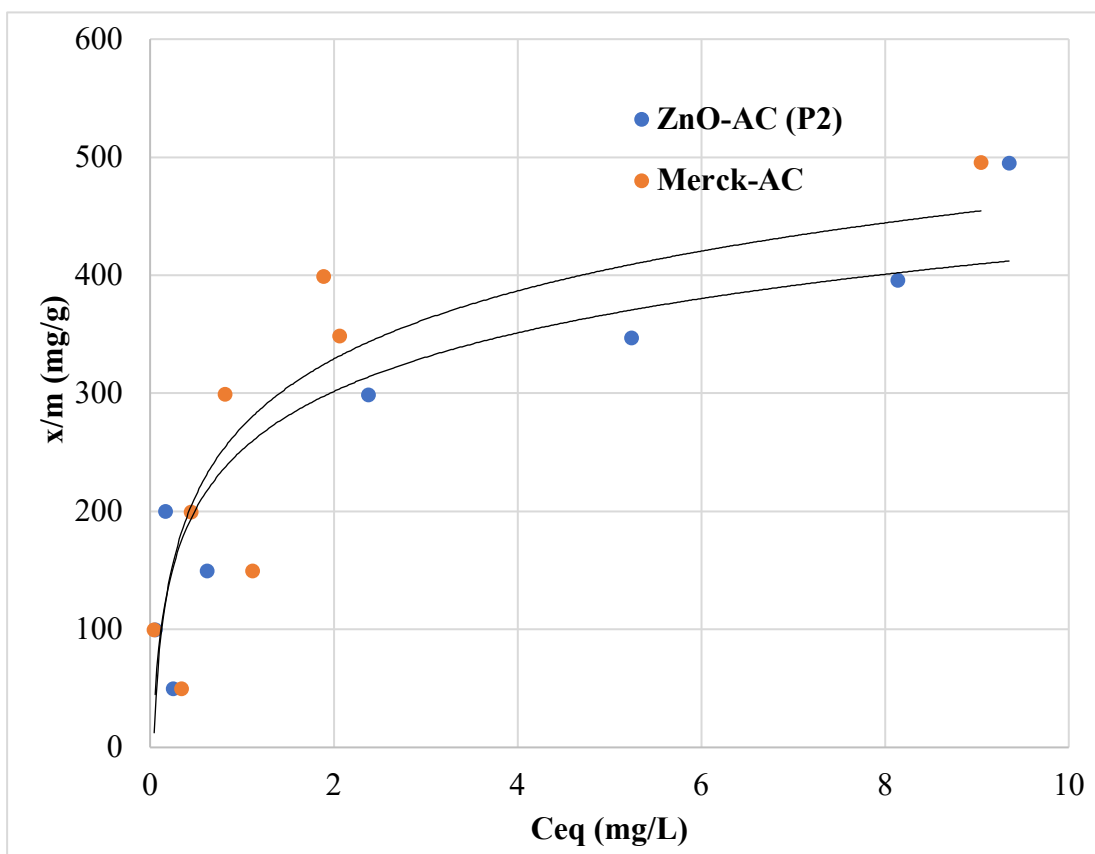

Figure 12. Adsorption isotherms of methylene blue on the commercial activated carbon and modified one Protocol 2.

CHAPTER III: RESULTS AND DISCUSSION

Table 08. Langmuir's equations and constants for the adsorption of methylene blue on the two activated carbons.

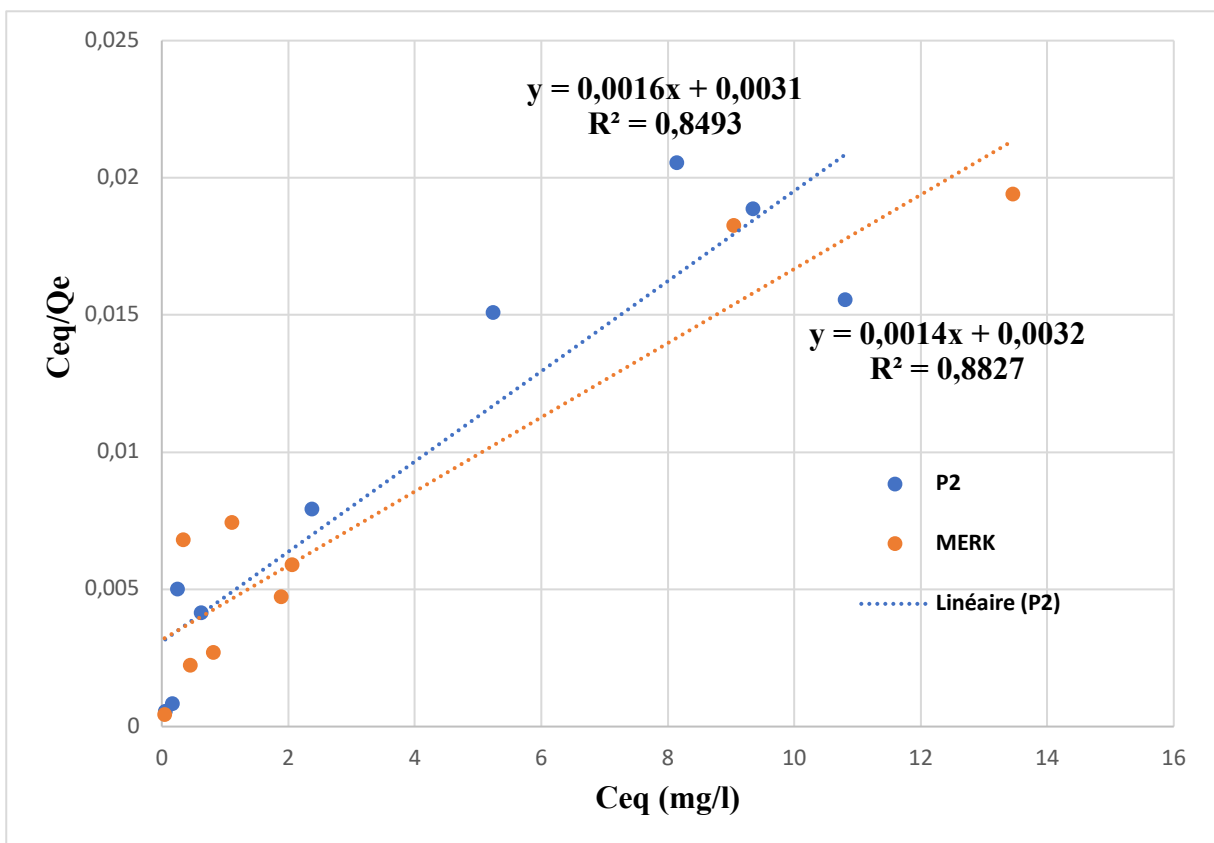| Adsorbent	Mathematical model	Langmuir equation	R^2	K_L (L/mg)	b (mg/g)	S_{BM} (m²/g)
Merck-AC	Linear	$C_{eq}/q_e = 0.0014\,C_{eq} + 0.0032$	0.88	0.4375	714.28	1600.54
ZnO-AC (P2)	Linear	$C_{eq}/q_e = 0.0016\,C_{eq} + 0.0031$	0.84	0.516	625.0	1401.11

Figure 13. Linearized Langmuir isotherms for the adsorption of methylene blue on two activated carbons.

Table 09. Freundlich equations and constants for the adsorption of methylene blue on the two activated carbons.

Adsorbant	Mathematical model	Freundlich equation	R^2	Kf (L/mg)	n (mg/g)
Merck-AC	Linear	$Logq_e = 0.3941\ LogC_{eq} + 2.3499$	0.66	223.82	0.42
ZnO-AC (P2)	Linear	$Logq_e = 0.3601\ LogC_{eq} + 2.3226$	0.73	210.18	0.43
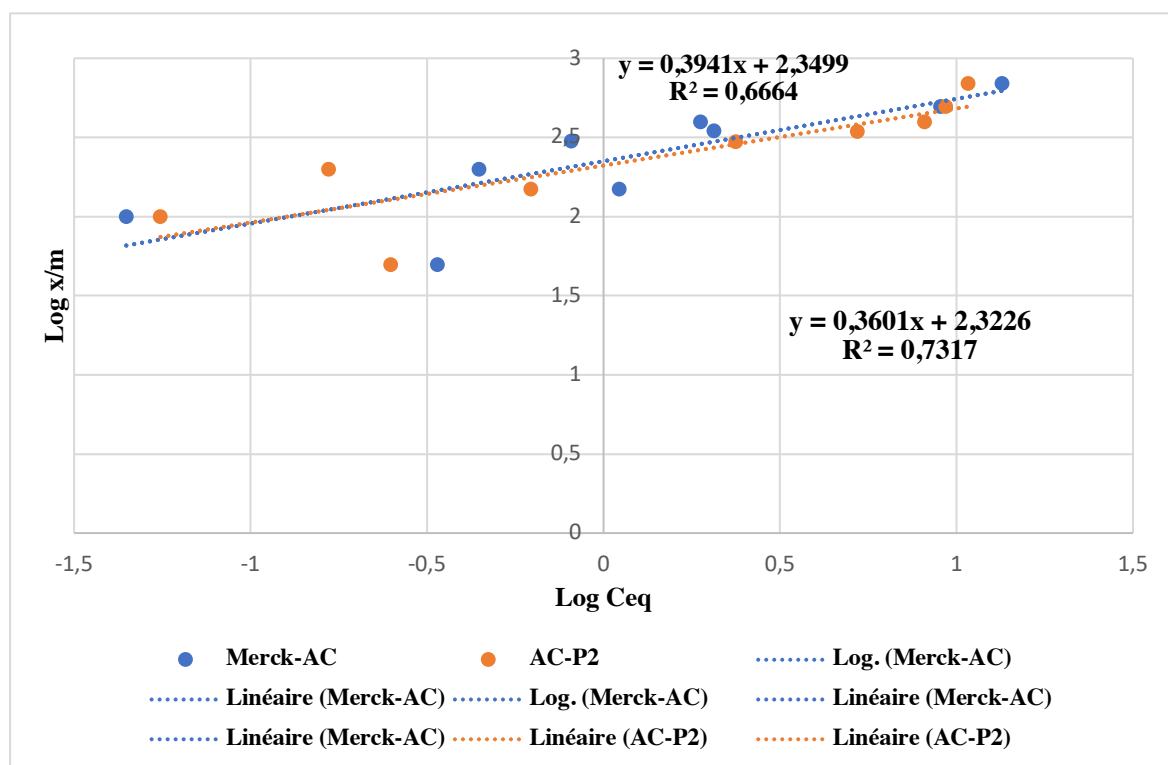
Figure 14. Linearized Freundlich isotherms for the adsorption of methylene blue on two activated carbons.

The adaptation of the Langmuir model for the two systems is shown in Figure 12 with satisfactory correlation coefficients. The adsorption results were processed using the linear Langmuir relation with these constants K_L (L/mg) and b (mg/g) as obtained from the slopes and intercepts in Table 8. and that resulted in different K_L constants. The linear model better reflects

the data obtained. K_L takes a value of 0.43 for Merck activated carbon and 0.51 for modified activated carbon. These K_L values indicate that Merck activated carbon and modified one exhibit similarity in energy factors for methylene blue adsorption. The adsorption capacity for activated carbons from Merck and modified are 714.28 and 625.0 mg/g respectively. The Freundlich model does not describe the adsorption of methylene blue on the two activated carbons studied because the correlation coefficient is low as it is shown in Figure 14 and Table 9. We can say that the strong adsorption of methylene blue on Merck and modified activated carbon is probably due to the presence of increased porosity, the pores being characterized by their decolorizing power towards colored pigments such as the blue of methylene.

Therefore, our activated carbon produced in the laboratory has a decent affinity for this dye. This Large capacity on the complex surface of the activated carbon can also be explained by ion exchange between the adsorbent and the adsorbate.

General conclusion

Preparation and characterization of AC-ZnO-NP were the main aims of this study. The first part consisted of preparing activated carbons (P1 and P2) from metallic nanoparticles of ZnO using different protocols. In the second part, we studied different ways of characterizing the surface of prepared activated carbon. Starting with the index value for characterizing the microporosity of activated carbons. The value obtained for modified activated carbon in protocol 2 is 1145.11 mg/g, indicating high microporosity. In the case of activated carbons from Merck and Protocol 1, their values are 987.98 and 678.496 mg/g respectively, lower than P2-prepared carbon. The second method is Boehm's method for characterizing the surface charge of activated carbons, revealing a higher equivalent mass and carboxyl groups in the P2-prepared carbon. FTIR analysis confirms these results. The Boehm method enables us to identify signals which characterize the acid functions. The pH point of zero charge values of the majority of manufactured carbons prepared P1 and P2 and Merck are below 8, indicating the slightly acidic nature of the surface of these materials. and Last but not least, the value of the methylene blue index method, which evaluates the mesoporosity of the Merck material and how higher it is than the prepared activated carbons with a result of (231.806 mg/g). The equilibrium data are analyzed using Langmuir, Freundlich, and Temkin isotherm equations. The result shows that the experimental data are best correlated by Langmuir isotherm. The last part is devoted to the adsorption of methylene blue. It is clear that AC Merck, and AC-ZnO, were efficient sorbents with a high adsorption capacity for the removal of MB and it can be proposed for the removal of these dyes from aqueous solutions. Nevertheless, the impact of pH, the mass, the temperature, and the duration of the reaction play a role in the effectiveness of the modified activated carbon 2, and studying these factors can make the AC-ZnO more favorable and efficient for other adsorption of dyes.

REFERENCES

[01]   Nasrollahzadeh, M.S., Hadavifar, M., Ghasemi, S.S. and Arab Chamjangali, M.
        (2018).   Synthesis of ZnO nanostructure using activated carbon for photocatalytic
        degradation of methyl orange from aqueous solutions. *Applied Water Science*, 8(4).
        doi: https://doi.org/10.1007/s13201-018-0750-6.

[02]   M Doi. TANG, ROGER BACON, Pyrolysis in Organic Chemicals from Biomass,
        Carbon 2, (1964) 211-20.

[03]   M. SLASLIA, M. JORGE, F. STOECKLI, N A. SEATON, Modelling of water
        adsorption by activated carbons: effects of microporous structure and oxygen content,
        Carbon 42, (2004) 1947-1952.

[04]   Manivannan, A., Chirila, M., Giles, N.C. and Seehra, M.S. (1999). Microstructure,
        dangling bonds and impurities in activated carbons. *Carbon*, [online] 37(11), p.1741.
        Available at:
        https://www.academia.edu/24558347/Microstructure_dangling_bonds_and_impurities
        _in_activated_carbons [Accessed 12 Jun. 2023].

[05]   Bentarfa, D., Ed, P. and Sekirifa, L. (n.d.). Preparation and characterization of
        activated carbon from date palm fibers: application as adsorbents and super capacity.
        [online] Available at: https://dspace.univ-
        ouargla.dz/jspui/bitstream/123456789/30409/1/These%20bentarfa%201%20A_compr
        essed_compressed.pdf.

[06]   Bentarfa, D., Ed, P. and Sekirifa, L. (n.d.). *Preparation and characterization of
        activated carbon from date palm fibers: application as adsorbents and super capacity*.
        [online] Available at: https://dspace.univ-
        ouargla.dz/jspui/bitstream/123456789/30409/1/These%20bentarfa%201%20A_comp
        essed_compressed.pdf.

[07]   Ep, R. and Bellaterra, Y. (2013). *Removal of water pollutants by adsorption on
        activated carbon prepared from olive- waste cakes and by biological treatment using
        ligninolytic fungi*. [online] Available at:
        https://www.tdx.cat/bitstream/handle/10803/131275/rbey1de1.pdf?sequence=1.

[08]   Nagar, N. (2018c). *Synthesis of Metal Nanoparticles and Their Application in
        Degradation of Textile Dyes by Advanced Oxidation Process*. [online] Available at:
        https://www.uok.ac.in/notifications/Full%20thesis%20Niharika%20Chemistry.pdf.

[09]   Shah, N., Gul, M., Abbas, M., Amin, D., 2020. Synthesis of Metal Oxide
        Semiconductor Nanostructures for Gas Sensors.
        https://doi.org/10.5772/intechopen.86815

[10]   El Hamidi, A., El Mahboub, E., Meziane, K., El Hichou, A., Almaggoussi, A., 2021.
        The effect of electronegativity on optical properties of Mg doped ZnO. Optik 241,
        167070. https://doi.org/10.1016/j.ijleo.2021.167070

[11]   B. Pant, M. Park, H.Y. Kim, S.J. Park, Ag-ZnOphotocatalyst anchored on carbon
        nanofibers: Synthesis, characterization, and photocatalytic activities, Synth. Met., 220
        (2016) 533-537.

[12]   K. Mouhli, K. Taraft, élaborationdescouchesmincesdeZnOetde ZnO : Alpar le
        procédésolgel, mémoire DEA, UniversitédeBejaia, 2010.

[13]   Ayawei, N., Ebelegi, A.N., Wankasi, D., 2017. Modelling and Interpretation of
        Adsorption   Isotherms. Journal of Chemistry 2017, e3039817.
        https://doi.org/10.1155/2017/3039817

[14]   Mudhoo, A., Beekaroo, D., 2011. Adsorption of Reactive Red 158 Dye by
        Chemically Treated Cocos Nucifera L. Shell Powder: Adsorption of Reactive Red 158
        by Cocos Nucifera L. Springer Science & Business Media.

[15]   T. M. Elmorsi, "Equilibrium isotherms and kinetic studies of removal of methylene
        blue dye by adsorption onto miswak leaves as a natural adsorbent," *Journal of
        Environmental Protection*, vol. 2, no. 6, pp. 817–827, 2011.

[16]   A. Günay, E. Arslankaya, and I. Tosun, "Lead removal from aqueous solution by
        natural and pretreated clinoptilolite: adsorption equilibrium and kinetics," *Journal of
        Hazardous Materials*, vol. 146, no. 1-2, pp. 362–371, 2007

[17]   A. Dąbrowski, "Adsorption—from theory to practice," *Advances in Colloid and
        Interface Science*, vol. 93, no. 1–3, pp. 135–224, 2001.

[18]   Meroufel, B., Benali, O., Benyahia, M., Benmoussa, Y. and Zenasni, M. (2013).
        Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin:
        Characteristics, isotherm, kinetic and thermodynamic studies. *J. Mater. Environ. Sci*,
        [online] 4(3), pp.482–491. Available at :
        https://www.jmaterenvironsci.com/Document/vol4/vol4_N3/60-JMES-361-2013-
        Meroufel.pdf.

[19]   Ragadhita, R., Nandiyanto, A., 2021. How to Calculate Adsorption Isotherms of
        Particles Using Two-Parameter Monolayer Adsorption Models and Equations.

Indonesian Journal of Science and Technology 6, 205–234.
https://doi.org/10.17509/ijost.v6i1.32354

[20]   Site web: http://www.chemical-engineering-design.com

[21] Huameicarbon. (n.d.). *Welcome*. [online] Available at:
https://www.huameicarbon.com/main-indicators-of-activated-carbon/ [Accessed 12
Jun. 2023].

[22]   V. Minkova, S.P. Marinov, R. Zanzi, E. Bjornbom, T. Budinova, M. Stefanova, L.
Lakov. Thermochemical treatment of biomass in a flow ofsteam or in a mixture of
steam and carbon dioxide. *Fuel Processing Technology*, 62, 45–52. (2000).

[23]   Ecologix Envirommental systems LLC 120 Ansley way Roswell GA, 30075. *Glossary
of termes commonly used with activated carbon.*

[24]   Charbon actif haute qualité T2. (n.d.). Available at:
http://www.silexinternational.com/produits/traitement/pdf/16-charbon-haute-
qualite.pdf [Accessed 12 Jun. 2023].

[25]   O.A. Ekpete, M. Horsfall, Kinetic sorption study of phenol onto activated carbon
derived from fluted pumpkin stem waste (Telfairia occidentalis Hook. F), ARPN J.
Eng. Appl. Sci. 6 (2011) 43–49).,

[26]   O.S. Bello, K.A. Adegoke, O.O. Akinyunni, Preparation and characterization of a
novel adsorbent from Moringa oleifera leaf, Appl. Water Sci. 7 (2017) 1295–1305)

[27]   M. Hadi, M.R. Samarghandi, G. McKay, Equilibrium two-parameter isotherms of acid
dyes sorption by activated carbons: study of residual errors, Chem. Eng. J. 160 (2010)
408–416.)

[28]   S. Nethaji, A. Sivasamy, A.B. Mandal, Adsorption isotherms, kinetics and mechanism
for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared
from Juglans regia shell biomass, Int. J. Environ. Sci. Technol. 10 (2013) 231–242)

[29]   M.A. Ahmad, N.A. Ahmad Puad, O.S. Bello, Kinetic, equilibrium and thermodynamic
studies of synthetic dye removal using pomegranate peel activated carbon prepared by
microwave-induced KOH activation, Water Resour. Ind. 6 (2014) 18–35.).

[30]   Ghazy, M., Askalany, A., Kamel, A., Khalil, K.M.S., Mohammed, R.H. and Saha,
B.B. (2021). Performance enhancement of adsorption cooling cycle by pyrolysis of
Maxsorb III activated carbon with ammonium carbonate. *International Journal of
Refrigeration*, 126, pp.210–221. doi:https://doi.org/10.1016/j.ijrefrig.2020.12.036.