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Presented by:

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Subject:

**Valorization and using of mining waste from  
Djebel Onk (TEBESSA) for the synthesis of  
nano-composites**

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﴿قُلْ هَلْ يَسْتَوِي الَّذِينَ  
يَعْلَمُونَ وَالَّذِينَ لَا يَعْلَمُونَ إِنَّمَا يَتَذَكَّرُ أُولُو  
الْأَلْبَابِ﴾

(سورة الزمر الآية 9)

صدق الله العلي العظيم

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# Dedication



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The journey was neither short nor the road fraught with facilities, but I did it With love, I dedicate the fruit of my success and graduation

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# Dedication

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I dedicate my efforts and the fruit of my labor

To **my mother**, the light of my existence and my angel in life

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### Abstract

Nanotechnology is a multidisciplinary field, as it combines the knowledge of different disciplines: Chemistry, physics, biology... We conducted a study to evaluate the catalytic activity of nanocomposites found in medicinal plants by utilizing minerals found in varying proportions in mineral residues from the phosphate mining process in the neck mountain mine instead of resorting to synthesized minerals, Therefore, we investigated the properties of peppermint plant and synthesized nanocomposites extracted from peppermint plant extract, the properties of these compounds were studied using UV-Vis, XRD, FTIR and bacterial activity.

We concluded that HD-NC is a good catalyst for many reactions, resistant to pollution and has a role in the environment.

**Keywords :** mint plant, green synthesis, metal waste, nanocomposites.

### المخلص

تعد تقنية النانو مجال متعدد التخصصات، لأنها تجمع بين معرفة تخصصات مختلفة: الكيمياء والفيزياء والبيولوجي ... إلخ ، قمنا بدراسة لتقييم النشاط التحفيزي للمركبات النانوية المتواجدة في النباتات الطبية باللجوء إلى المعادن الموجودة بنسب متفاوتة في المخلفات المعدنية من عملية تعدين الفوسفات في منجم جبل العنق بدل اللجوء إلى المعادن المصنعة ، ولذلك قمنا بالدراسة حول خصائص نبتة النعناع وتوليف المركبات النانوية المستخرجة من مستخلص نبتة النعناع ، تم دراسة خصائص هذه المركبات باستخدام الأشعة فوق البنفسجية والمرئية **vis-UV** والأشعة السينية **XRD** و مطياف الأشعة تحت الحمراء **FTIR** والنشاط البكتيري.

توصلنا إلى أن **HD-NC** محفز جيد لكثير من التفاعلات ومقاوم للتلوث وله دور في البيئة.

**الكلمات المفتاحية :** نبتة النعناع ، التوليف الأخضر ، المخلفات المعدنية ، المركبات النانوية .

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## List of abreviations

<b>Å</b>	Angstrom (unit for measuring distance)
<b>AFM</b>	Atomic Force Microscope
<b>ATCC</b>	L' American type culure collection
<b>BRGM</b>	Bureau de recherches géologiques et minières
<b>CVD</b>	Chemical Vapor Deposition
<b>DNA</b>	Deoxyribonucleic Acid
<b>DTA</b>	Differential thermal Analysis
<b>EREM</b>	Enterprise de recherche et des études minières
<b>FERPHOS</b>	Entreprise national du fer et phosphate
<b>FTIR</b>	Fourier Transform Infrared Spectroscopy
<b>Hc</b>	Combustion heat
<b>HD NC</b>	ZnO/CuO/Cu <sub>2</sub> MgO <sub>3</sub>
<b>HRR</b>	Heat Rate Release
<b>IBM</b>	International Business Machines
<b>keV</b>	Kilo electron volt
<b>MEMS</b>	Electromechanical Microsystems
<b>NC</b>	Nanocomposite
<b>nm</b>	Nano meter
<b>NNI</b>	National Nanotechnology Initiative
<b>NPs</b>	Nanoparticles
<b>PDDS</b>	Nano composite with 4,4'-diaminodiphenyl sulfone matrix and reinforcement
<b>pH</b>	Hydrogen potential
<b>PMMA</b>	Poly methyl methacrylate
<b>PVD</b>	Physical Vapor Deposition
<b>SEM</b>	Scanning Electron Microscopy
<b>SOFREMINES</b>	Société Française d'études Minières
<b>SONAREM</b>	Société nationale de recherches et d'exploitation des ressources minières
<b>STM</b>	Scanning Tunneling Microscope
<b>TEM</b>	Transmission Electron Microscopy
<b>TGA</b>	Thermogravimetric Analysis
<b>TPL</b>	Tribasic Phosphate of Lime
<b>UV-vis</b>	Ultraviolet visible spectrometer
<b>XRD</b>	X-ray Diffraction
<b>µm</b>	Micro meter
<b>λ</b>	X-ray wavelength

## **General Introduction :**

Today, the emergence of nanoscience and nanotechnology represents one of the most promising developments in the material sciences, focusing on the design, characterization, production and application of materials and products obtained by controlling structure, shape and size on the nanometric scale (1 to 100 nm). These materials present new, more advantageous and unique physico-chemical properties that are very different from those of the same material in the bulk or atomic state.[1]

In recent years, the manufacture and use of nanomaterials has become an essential technology with applications in many industrial sectors. Nanocomposites, because of their specific electrical, optical, magnetic, chemical and mechanical properties, are currently used in many high-tech fields, such as the medical sector for diagnostics, antimicrobial and drug delivery [2], as well as in the electronics and optoelectronics industry or in the chemical sector for catalysis [3]. for environmental protection and energy conversion. [4]

The synthesis of nanocomposites is dominated by several physical and chemical methods. Physical methods generally require high temperatures and expensive equipment, which can limit potential industrial applications, especially those requiring large-scale production. Chemical methods, on the other hand, are costly and harmful for mass production [5]. For example, these methods often result in the adsorption of certain toxic chemical species onto the surface, which can have undesirable effects in medical applications.[6]

For several years now, the scientific community has been investigating other environmentally-friendly ways of synthesizing nanocomposites without using toxic substances. These include the green synthesis method, which uses living organisms (bacteria, fungi, yeast, plants, etc.) as bioreactors to synthesize nanocomposites. These methods have attracted a great deal of interest due to their ease of use, the availability of raw materials and, above all, their biological activity.

The phosphate deposits from Djebel Onk - Tebessa, are an important natural resource that receives wide economic interest, and phosphate ore is processed in two ways: The first is wet processing and the second is dry processing, and the waste of this processing occupies large areas in the region without benefit, which constitutes harm to the environment and living organisms .

This is what brought to our minds the idea of exploiting these industrial wastes because they contain large proportions of various metals such as  $P_2O_5/MgO$  and others.[7] By using them as a local, natural and sustainable source of metals in the process of synthesizing nanocomposite, this project is expected to have positive effects on the environment, in order

to achieve a balance between the exploitation of natural resources and environmental protection at the same time.

The goal here is to replace manufactured minerals with natural minerals found in the tailings of the Djabel Onk mine in Tebessa in the biosynthesis of nanocomposite from the extract of a medicinal plant rich in active compounds, mint, which is a simple, fast, and environmentally safe process, [8]from this point of view we can summarize the issue of our research in: **How can we replace manufactured minerals with minerals found in mining waste (Djabel Onk - Tebessa) in the green synthesis of nanocomposites?**

To answer this question, we divided the note into 3 chapters:

-Chapter 1: " General information on nanomaterials "

It includes their definition, properties, classification, and applications in various fields .

-Chapter 2: "Characterization and Preparation Methods"

It was represented in the physical and chemical methods of manufacturing nanocomposite and their characterization methods from X-ray, infrared, UV-visible, and scanning electron microscopy techniques ... etc.

- Chapter 3: "Synthesis, Results and Discussion" during which we addressed the experimental stages in the synthesis of nanocomposites and discussed the results obtained.

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# **Chapter I: General information on nanomaterials**

## 1. Nano history:

People have been exploiting nanotechnologies for thousands of years, notably in the manufacture of steel and the vulcanization of rubber. The first distinctive concepts of nanotechnology were mentioned as early as 1867 by James Clerk Maxwell. [1]

By the 1930s, our understanding of atoms, molecules and intermolecular forces was well forces was well developed. Loschmidt estimated that atoms had a size of around 1 nanometre, which was close to reality. Observation of matter on the nanometric scale nanoscale began very early on, and the invention of the electron microscope in 1930 was a major breakthrough, enabling direct observation at this scale. [2][3]

The idea of nanotechnology is attributed to Nobel laureate Richard Feynman, who delivered a highly acclaimed and groundbreaking speech in 1959 (published in 1960) at one of his conferences-.one of his lectures. Feynman declared: "As far as I know, the principles of physics are not opposed to the possibility of manipulating things atom by atom". At Feynman's words were initially seen as pure science fiction.

Today, we have instruments that precisely realize his prediction: to create structures by manipulating individual atoms.[4][5]

The term "nanotechnology" was originally coined by Norio Taniguchi of University of Science in Tokyo in a 1974 research paper, defining it as follows: "Nanotechnology is essentially the manipulation, separation, assembly and deformation of materials by an atom or molecule. Since then, the definition of nanotechnology has generally been extended to include dimensions 10 nanometers.[1]

The advance of nanotechnology owes much to the invention of two analytical tools that have revolutionized the imaging of nanoscale surfaces: the scanning tunneling microscope (STM) and the atomic force microscope (AFM). Capable of imaging surfaces with atomic resolution, these two instruments were invented by "Gerd Binnig" and "Heinrich Rohrer" of IBM Zürich in 1981, for which they were awarded the Nobel Prize in Physics in 1986 These tools effectively opened the doors to the nanoworld. With the introduction of STMs, scientists not only acquired the ability to image surfaces with atomic atomic precision, but also to manipulate individual atoms.[6]

## 2. Nanocomposites:

### 2.1. Definition :

Nanocomposites encompass a wide variety of materials composed of two or more at least one of which has dimensions in the nanometer range, generally between 1 and 100 nm. Nanocomposites comprise two phases, such as a nanocrystalline phase nanocrystalline phase and a matrix phase. These phases can be combinations of inorganic- inorganic, inorganic-organic or organic-organic materials. nanocomposite refers to the incorporation of nanometric particles, such as metals metals, semiconductors, dielectric materials, etc., in various matrix materials, including including ceramics, glass and polymers.[7]

### 2.2. Types of nanocomposites :

Nano-composites can be obtained by integrating clays in a polymer matrix , depending on the constituents used:

#### 2.2.1. Micro-composites :

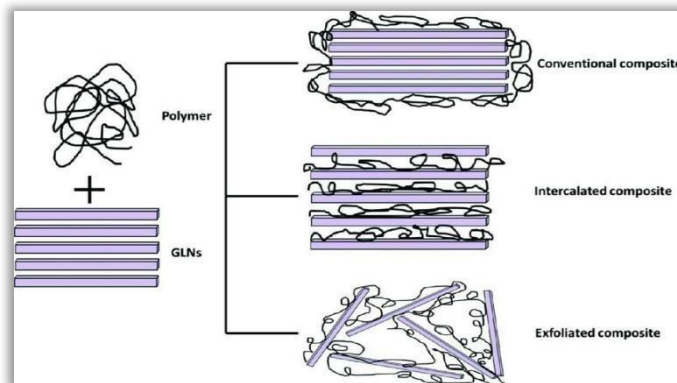
The polymer does not intercalate between the clay layers, resulting in separation of the immiscible phases .of immiscible phases, generally with properties similar to those of micro-composites.[8]

#### 2.2.2. Intercalated nanocomposites :

Are characterized by the insertion of one or more polymer chains between the clay layers forming a relatively ordered and expanded inorganic lamellar structure, inorganic lamellar structure. [8]

#### 2.2.3. Exfoliated nanocomposites :

Distinguished by the uniform dispersion of the delaminated clay layers in the polymer matrix , This delamination strengthens polymer/clay interactions, considerably the contact surface and conferring specific properties to this type of nanocomposite ,nanocomposites.[8]



**Figure I.1:** Schematic representation of the different morphologies of nanocomposites, (1) microcomposite (2) intercalated nanocomposite (3) exfoliated nanocomposite.[9]

### 2.3. Nano-composite classification:

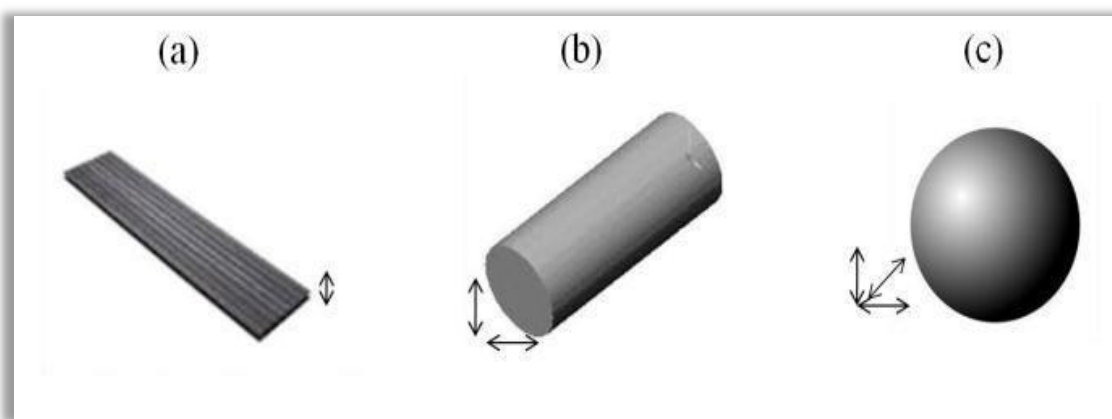
#### 2.3.1. Classification according to the nature of the matrix :

We can apply the classic classification of composites according to the nature of the matrix in ascending order of service temperature:

- Composite materials with polymeric and organic matrices.
- Composite materials with a metal matrix.
- Composite materials with a ceramic matrix.[10]

#### 2.3.2. Classification according to nanofiller form (reinforcement) :

Nano-composites are classified according to the type of nanometric reinforcement used, A variety of reinforcements can be used.[11]



**Figure I.2:** The three categories of nanofillers: 1-dimensional (a), 2-dimensional (b) and 3-dimensional (c). [11]

##### 2.3.2.1. One-dimensional nanofillers (sheets):

These materials have two preferred directions .nanometer size in one direction, while the other two directions have micrometer micrometer dimensions. Clays are undoubtedly the best-known of these materials, due to their natural their natural character and ease of extraction.[12]

##### 2.3.2.2. Two-dimensional nanofillers (nanofibers) :

These particles have two dimensions at the nanometric scale, while the third is much larger, like carbon nanotubes known for their exceptional mechanical and electrical properties. They can be integrated into polymer matrices such as polyamide and polyester, where their distribution affects properties. The addition of these particles increases polymer viscosity, but to a lesser degree than traditional fibers. [13]

##### 2.3.2.3. Three-dimensional nanofillers (nanoparticles):

These nanometric particles, with diameters ranging from 30 to 150 nanometers, include atomic aggregates, metallic nanoparticles and fullerenes. They are added to improve optical, electrical and magnetic properties. [13]

## 2.4. Properties of nanocomposites:

### 2.4.1. Mechanical properties:

"Mechanical properties" refers to stiffness and flexibility. Rigid polymers may lack sufficient rigidity. Adding rigid fillers such as fiberglass makes composites stiffer but less flexible. [14]

### 2.4.2. Thermal properties:

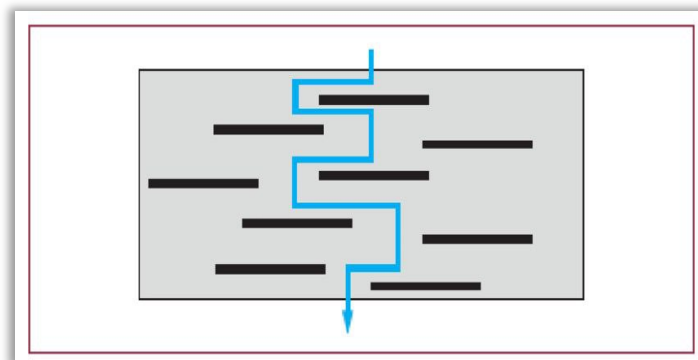
Thermal stability of the polymers is assessed by thermogravimetric analysis. The addition of exfoliated lamellar silicates increases the degradation temperature of polymers, enabling them to be used at higher temperatures. This improvement depends on the dispersion of the filler in the polymer.[15]

### 2.4.3. Fire properties:

Reducing flammability is crucial for polymers used in construction and transportation. Traditional flame retardants are expensive and no longer meet global environmental standards.[17] Polymer matrices reinforced with silicate sheets offer improved fire resistance, attracting great interest. The main method for assessing fire properties is the cone calorimeter, measuring heat release rate (HRR), heat of combustion (Hc), and carbon monoxide and smoke production. HRR, particularly its peak, is the most significant parameter of fire resistance.[16][18]

### 2.4.4. Barrier properties :

Nanometric fillers have a significant impact on the barrier properties of polymer matrices. The addition of lamellar nanometric fillers to a polyamide matrix considerably reduces permeability to oxygen, hydrogen and water vapor, by up to 10 times compared to the polymer without these fillers [19][20]. This reduction is due to the creation of a fine network by the nanometric fillers, which impedes the diffusion of gaseous molecules through the polymer structure. The integration of solid nanometric particles forces all molecules to circulate in a complex manner around these particles, disrupting their movement through the composite structure.[21]



**Figure I.3:** Tortuosity of the path of molecules diffusing through a nanocomposite film.[22]

**2.4.5. Optical properties :**

These materials stand out for their unique properties, offering a wide range of applications. Despite their electrical charge, they are exceptionally transparent, appearing to be 10 to 100 times thicker than they really are. This transparency, combined with solid mechanical properties, is a crucial advantage in fields such as packaging. Furthermore, in sectors such as light guides, layered reinforced nanocomposites are being explored for applications such as optical fibers, joints and sensors. [23]

**2.4.6. Rheological properties :**

After the addition of the nanometric filler, understanding polymer rheology becomes crucial for composite processability. In general, the viscosity of nanoscale composites increases at low shear rates and with increasing filler concentration, often similar to the behavior of solids, attributed to physical stacking or percolation of silicate layers. At high shear rates, a decrease in viscosity is observed, suggesting alignment of the silicate layers in the direction of flow.[24][25]

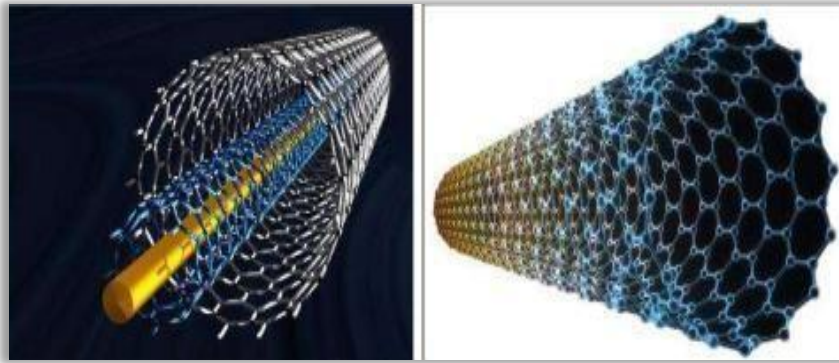
- Other properties have also been demonstrated Electrical and catalytic properties.

**3. Nanomaterials :****3.1. Definition :**

Nanomaterials are solid structures characterized by extremely small dimensions generally on the nanometer scale. Pomogailo classifies them according to whether they have one, two or three dimensions. [26]

**3.2. Nanomaterial forms:****3.2.1. Carbon nanotubes :**

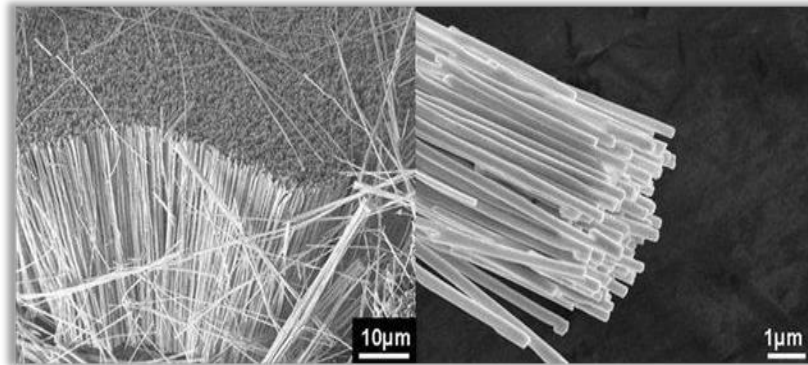
Carbon nanotubes are hollow cylinders of carbon atoms arranged in a hexagonal pattern, with diameters ranging from 0.7 nanometres to several millimetres long. They can be metallic or semiconducting, and conduct very high current densities. They are lightweight, mechanically durable, excellent thermal conductors, possess unique electronic properties and high molecular adsorption capacity, as well as high chemical and thermal stability.[27]



**Figure I.4:** Carbon nanotubes.[28]

### 3.2.2. Nanowires:

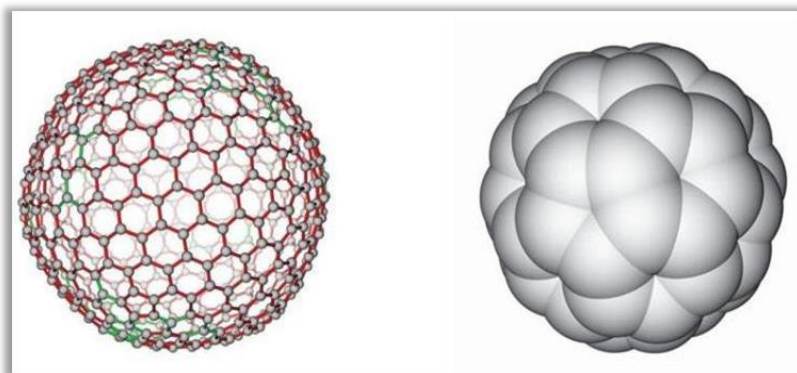
Nanowires, a few tens of nanometers in diameter and with a high length-to-diameter ratio, can conduct electricity or act as semiconductors. Made from various materials such as silicon, cobalt, gold and copper, they are used in nanoelectronics to transport electrons.[27]



**Figure I.5:** Nanowires. [29]

### 3.2.3. Nanobills :

Nanospheres belong to the fullerene family ( $C_{60}$ ), but with a slightly different composition, as they are multilayered and lack a center. At due to their onion-like layered structure, scientists have named them "buckyballs", in reference to onions. They can have a diameter of over 500 nanometers.[30]



**Figure I.6:** Nanobills .[30]

### 3.2.4. Fullerene :

Carbon nanoparticles, linked by triple bonds, have a spherical shape similar to graphite, but incorporate pentagons and sometimes heptagons, which curve the layers to form spherical or cylindrical structures.[30]

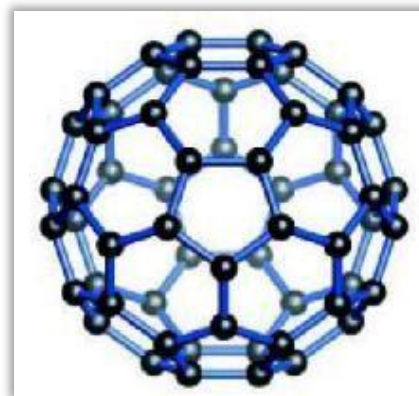


Figure I.7: Fullerene C60.[27]

### 3.2.5. Quantum wells:

Quantum wells are spherical nanocrystals from 1 to 10 nm in diameter, existing in various forms such as semiconductors and metals. Containing 1,000 to 100,000 atoms, they enable the wavelength of emitted light to be adjusted by modifying their dimensions.[30]

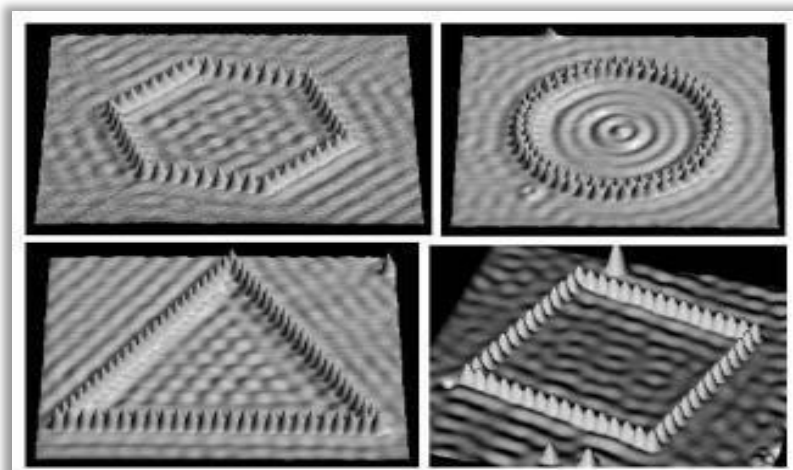
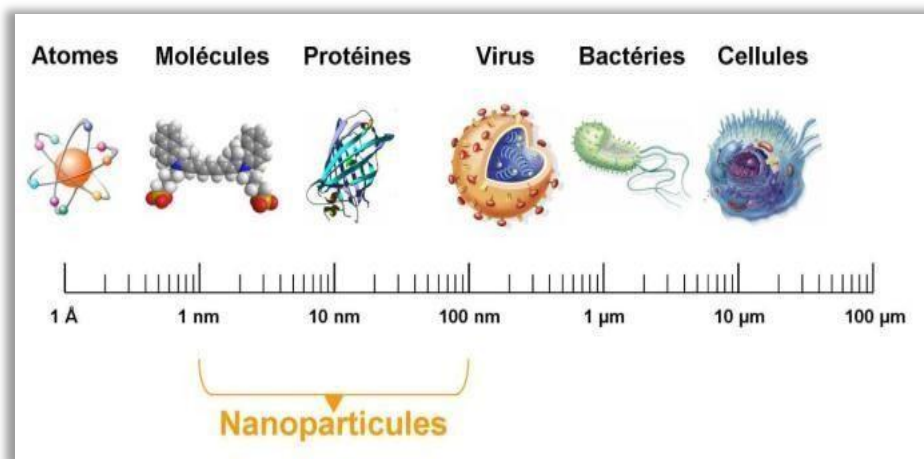


Figure I.8: Different shapes of quantum wells showing the organization of individual atoms.[27]

## 4 . Nanoparticles :

### 4.1. Definition:

Nanoparticles are small entities ranging in size from 1 to 100 nanometers. This definition does not emphasize shape, only size. By nanoparticles can take on many different shapes, including spherical rectangular or even angular in crystalline form. In some cases, particles have to be shaped using tools such as plasma torches, which reduce their size their size considerably, often resulting in a glassy state.[26]



**Figure I.9:**Size range of nanoparticles compared with those of the main chemical and biological structures.[31]

## 5. Nanotechnology :

### 5.1. Definition:

Nanotechnology involves the creation and manipulation of structures on the nanometer scale (1 to 100 nm), encompassing the preparation, characterization and control of atoms or molecules to develop materials with distinct properties. According to the NNI and the Royal Society, they focus on the design and application of precise structures at this scale to improve the properties of materials.[32][33][34]

### 5.2. Principles and benefits of nanotechnology :

The Principle	L' avantage
The ability to precisely control the movement of individual atoms and rearrange them.	The ability to construct any substance in the universe rests on the atom, which is the fundamental building block for all matter.
The physical and chemical properties of a substance change when it is reduced to the nanoscale, resulting in differences compared to the same substance at its natural scale	Nanotechnology is based on the principles of physics, chemistry, biology, electrical engineering and electronics.
Nanotechnology is based on the principles of physics, chemistry, biology, electrical engineering and electronics	Nanotechnology bridges the gap between scientific disciplines and encourages everyone, whatever their scientific speciality, to explore and participate in their respective fields, and to collaborate with others
The ability to control atoms in the	The properties of materials and machines are

manufacture of materials and machines, purifying them of impurities and eliminating defects	improving, becoming smaller, lighter, stronger, faster, more economical and more energy-efficient
The properties of materials and machines are improving: they are becoming smaller, lighter, stronger, faster, more economical and more energy-efficient.	The properties of materials and machines are improving: they are becoming smaller, lighter, stronger, faster, more economical and more energy-efficient

**Table I.1:** Principles and benefits of nanotechnology.[35]

### 5.3. Nanotechnology applications :

Nanomaterials technology is expected to trigger major industrial revolutions and scientific discoveries over the next two decades, radically changing aspects of life. Currently, unprecedented research and applications are being carried out in this field, particularly in developed countries, encompassing diverse industries such as medicine, electronics, environmental protection and renewable energies. Nanotechnology offers enormous benefits, such as improving the efficiency of medical devices, reducing the size of electronic devices, developing more efficient and less expensive construction materials, and increasing the efficiency of solar cells. It is also helping to produce stain-resistant nanotechnology clothing and improve fuel efficiency in cars. Nanotechnology is also used to protect the environment through sensors and filters, and in agriculture to improve soil fertility and increase crop productivity. [36]



**Figure I.10 :** Nanotechnology applications

#### 5.4. Future objectives for nanotechnology :

Nanometric technology offers promising applications in fields that have a direct impact on human life. have a direct impact on human life. As a result, the development of its products can take years, due to the experimentation and research required to produce treatments, foods or weapons. In addition, sectors such as textiles, electronics, communications and others have fantastic future prospects which could become a reality in the years to come.[35]

Domain	Future objectives
<b>Industry</b>	The manufacture of materials and tools with high precision, efficiency and unique properties.
<b>Electronics</b>	Reduce machine dimensions while increasing speed and capacity, and reducing energy consumption .
<b>Medical</b>	Development of extremely precise, fast and efficient diagnostic, analysis and processing devices.
<b>Pharmacy</b>	Improve existing drugs and develop new, more effective ones with fewer side effects.
<b>Transport</b>	Reducing the weight of means of transport to save energy and improve roads.
<b>Chemistry</b>	Development of tailor-made catalytic materials to speed up reactions and increase production .
<b>Energy</b>	Developing alternative and renewable energy sources and reducing dependence on fossil fuels such as oil and gasoline.
<b>Environment</b>	The manufacture of environmentally-friendly materials that reduce waste and enable recycling.
<b>Space</b>	The production of materials not manufactured on Earth that protect vehicles against cosmic radiation .
<b>Agricultural</b>	Materials that decompose to feed plants, destroy insects and modify plant genes.

**Table I.2:** Nanotechnology's future objectives[35]

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# **Chapter II: Preparation and Characterization methods**

## 1. Nanocomposite production processes :

Nanocomposites have properties distinct from those of bulk materials, appearing at a critical length scale generally below 100 nm. Whatever their composition, when they are reduced to sizes below 100 nm, each substance presents new characteristics. These properties can be deliberately manipulated by adjusting the size, composition and shape of nanoscale materials scale, making composite size the main characteristic of nanocomposites .[1]

Over the past decade, numerous techniques have emerged for the manufacture of nanomaterials. The choice of appropriate techniques depends on a number of factors, conditions and synthesis methods. From an industrial point of view, factors such as cost, time and reproducibility of synthesis are essential. In general generally speaking, two main approaches - bottom-up and top-down - are employed. Although both play an important role in nanocomposite production, each has its own advantages and disadvantages. Consequently, the choice between these approaches depends very much on the specific requirements of the project. [1]

### 1.1. Physical methods for nanocomposite synthesis :

#### 1.1.1. Thermal evaporation:

In this method, a metal target is evaporated using a heating resistor under inert gas pressure. In the 1980s, Sattler et al. pioneered the development to develop this method for producing antimony, bismuth and lead aggregates of controlled size.[2]

#### 1.1.2. Laser ablation:

In laser ablation, a high-energy laser beam is directed at a specific target vaporize part of it, then condense the resulting particles onto the surface of a specific material. Nanocrystals form when the particles released by the target from condense in the gas phase within a certain pressure range (0.5 to 100 millibars). The size of these particles depends on the nature of the charged gas, its pressure and the intensity of the laser pulses. In 1965, Smith and Turner were the first to use this technique to produce thin layers of various materials using a pulsed sapphire laser ( $\lambda=694$  nm). Since then, a number of 2-6 nm particles of iron, nickel and cobalt have been obtained in this way.[2]

#### 1.1.3. Sputtering:

Sputtering uses a plasma of ionized gas to eject atoms from a target material. which are then deposited on a substrate. The temperature of the substrate and the distance between target and substrate are crucial to controlling the process. Specific are used to protect composites from oxidation and control their growth.[2]

#### 1.1.4. Electrical discharge:

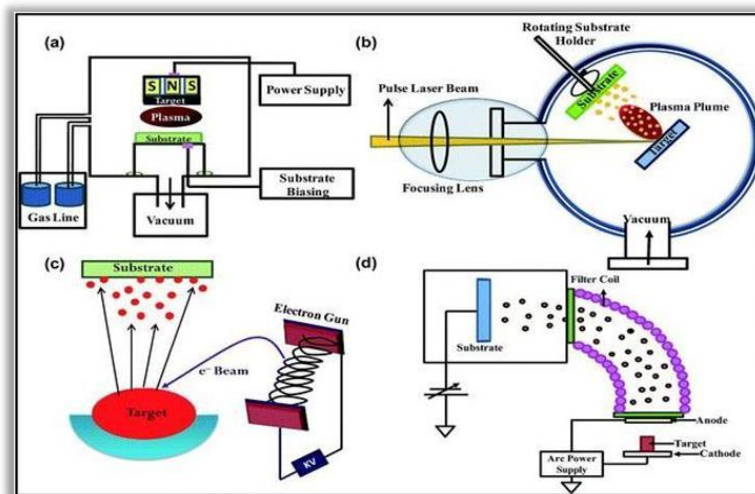
Creates an arc between two electrodes, evaporating the metal through a high-pressure helium jet to form aggregates deposited on the inner walls of the chamber. The size of the aggregates can be adjusted by controlling the speed of the helium jet, and the chemical composition can be altered by using different electrode materials for evaporation, enabling the structures such as nanotubes or fullerenes.[2]

#### 1.1.5. Ion implantation:

Ion implantation is a powerful physical method for producing nanocomposites embedded in a matrix. This technique has been used to synthesize magnetic nanocomposites in silica layers.[1]

#### 1.1.6. Physical Vapor Deposition (PVD):

Includes processes frequently used for the manufacture of nanocomposites and the deposition of thin layers of materials, generally ranging from a few nanometers to a few micrometers. It is an environmentally-friendly vacuum deposition method three main steps: (1) vaporization of the material from a solid source, (2) transport of the vaporized material, and (3) nucleation and growth, leading to the formation of thin films and nanocomposites.[3]

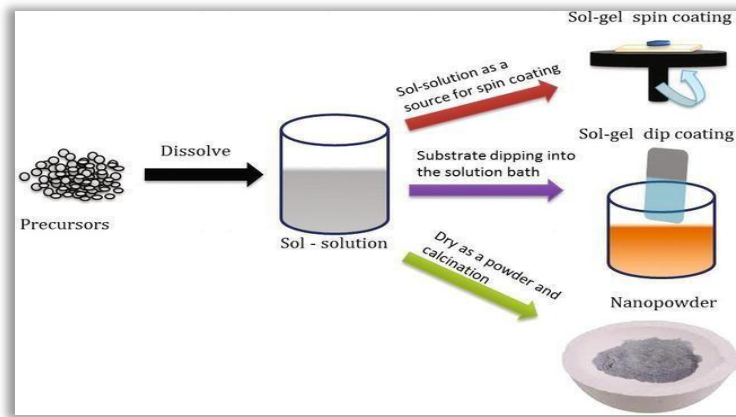


**Figure II.1:** Schematic representation of (a) sputtering, (b) electron-beam evaporation, (c) pulsed laser deposition and (d) vacuum arc technique.[3]

### 1.2. Chemical methods for nanocomposite synthesis :

#### 1.2.1. The sol-gel method:

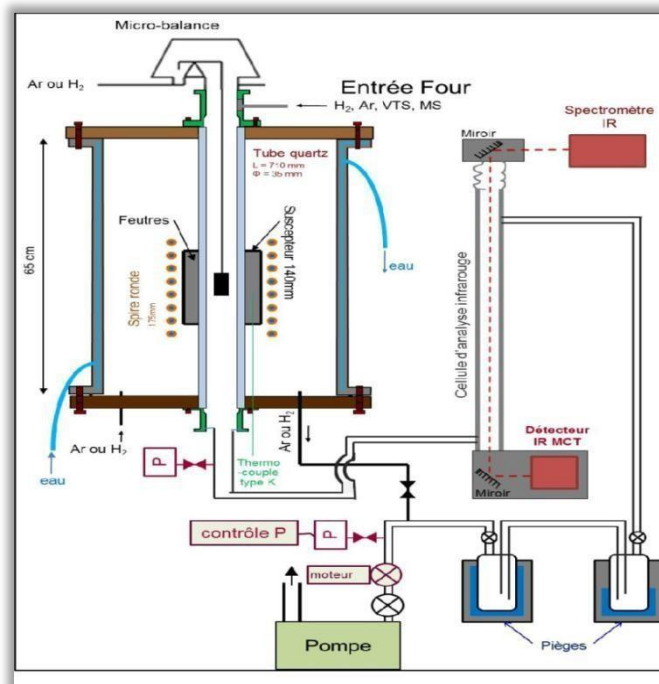
This section describes the manufacture of metal oxides from metal precursors. It involves hydrolysis of the precursors to form hydroxides, condensation of the hydroxides to form a gel, and finally, removal of the solvent and thermal heat treatments to obtain the desired metal oxide.[1]



**Figure II.2:** Sol-gel treatment diagram.[4]

### 1.2.2. Chemical Vapor Deposition (CVD) :

Chemical vapor deposition is a method used to manufacture thin films by depositing materials from gaseous precursors in a reaction chamber. Gas molecules combine in the chamber, and when the heated substrate comes into contact with these gases, a chemical reaction occurs, leading to the formation of a thin film on the substrate surface. Substrate temperature is a crucial element for controlling the CVD process.[5]



**Figure II.3:** Schematic diagram of the multi-instrument CVD reactor used.[3]

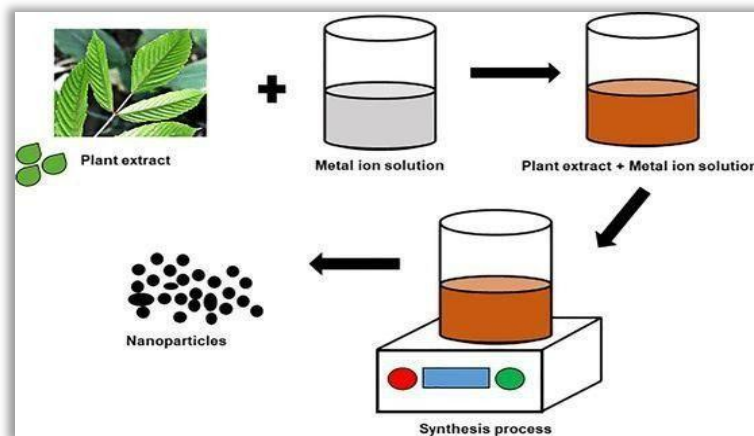
### 1.2.3. Thermal decomposition:

Thermal decomposition is a chemical process during which the bonds between compounds are broken by heat, leading to endothermic reactions. The temperature at which this occurs is called the decomposition temperature. Nanocomposites are produced by the thermal decomposition of metals at specific temperatures during chemical reactions, simultaneously generating by-products. [1]

### 1.3. Biological methods for nanocomposite synthesis :

#### 1.3.1. Plant extracts for nanocomposite synthesis :

The synthesis of nanocomposites from plant extracts is an environmentally friendly method, using natural materials to form nanocomposites of various types, including noble metals and metal oxides. This approach is fast, efficient and safe, making it suitable for a wide range of industrial and medical applications thanks to its environmental safety and high efficiency. [3]



**Figure II.4:** Schematic representation for plant-mediated biosynthesis of nanocomposites.

#### 1.3.2. Biomolecules as models for nanocomposite design :

Various biomolecules, including DNA, serve as models for synthesizing nanocomposites. DNA is particularly effective because it interacts strongly with transition metal ions. By creating a cross-linked DNA gel and adding transition metal ions, gold nanocomposites can be formed. This process involves the reduction of gold ( $\text{Au}^{3+}$ ), forming metal atoms and clusters that transform into nanocomposites along the DNA chain.[3]

## 2. Characterization techniques for nanocomposites :

Several analytical techniques are recommended for characterizing nanocomposite samples. These techniques provide comprehensive information on size, shape, crystallinity, charge and chemical composition of nanocomposites. The techniques used are UV-Visible spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).

## 2.1. Structural and morphological characterization :

### 2.1.1. X-ray diffraction (XRD) :

X-ray diffraction (XRD) is a non-destructive technique commonly used to characterize powdered solids, revealing their crystalline structures and the size of crystals in steel. Based on Bragg's law, it can be used to identify the crystalline phases of the catalyst, determine the average crystal size and study the structure of nanomaterials. However, it cannot provide information on the distribution or structural heterogeneity of nanocomposites.[6-7-8]

$$2d \sin(\theta) = n \lambda \quad (1)$$

$d$  = inter-lattice distance, i.e. distance between two crystallographic planes;

$\theta$  = half angle of deflection (half the angle between the incident beam and the direction of the detector direction);

$n$  = reflection order (integer);

$\lambda$  = X-ray wavelength.

Diffraction peaks are indexed according to Miller indices  $\{hkl\}$ , which represent crystallographic planes.

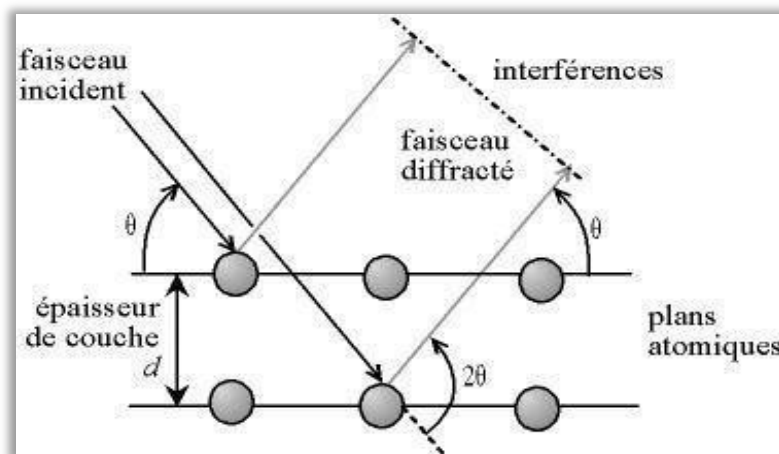


Figure II.5: Schematic diagram of Bragg's law principle.[9]

#### 2.1.1.1. Principle

X-ray diffraction is a technique used to analyze the crystalline structure of materials. When X-rays interact with a sample, they scatter in different directions, creating interferences that produce a diffractogram. Using Bragg's law, which relates the diffraction angle to the interatomic distances and wavelength of the X-rays, we can precisely identify the crystalline phases of the sample.[10]

### 2.1.1.2. Apparatus

Analyses were carried out by powder diffraction technique, using a Rigaku Ultima IV  $\theta/2\theta$  X-ray diffractometer, with copper  $K\alpha$  radiation ( $\lambda=0.154056$  nanometers). XRD images were recorded in the  $5 - 90^\circ$  range (in  $2\theta$ ) with an angular step size of  $0.02^\circ$ . To record the X-rays, it is necessary to grind the sample until it reaches a composite size of around 30 micrometers. The powder was then compressed onto the device's sample holder. The range observed ranges from 10 to 60 degrees.



**Figure II.6:** X-ray diffraction apparatus (Rigaku Ultima IV).

### 2.1.2. Scanning Electron Microscope (SEM) :

The Scanning Electron Microscope (SEM) produces images by scanning an electron beam over the sample, providing data on its topography and composition. Thanks to raster scanning, it offers a resolution of less than 1 nanometer, enabling detailed visualization at micro and nanoscales. In nanocomposite studies, SEM is crucial for analyzing dispersion, nanocomposite size and charge distribution in the matrix.[11]

#### 2.1.2.1. Principle

Scanning Electron Microscope (SEM) uses a focused beam of electrons a few kiloelectronvolts (keV) to scan a sample, providing high-resolution imaging. The primary electrons interact with the sample, producing secondary and backscattered electrons that are detected to form the image.

Backscattered electrons provide topographical information, while secondary electrons reveal chemical composition and surface structure. By using secondary electrons, the SEM scans the sample, producing images of its topography and composition.[12][13]

#### 2.1.2.2. Apparatus

In this study, SEM was used to examine PDDS and their nanocomposites, enabling their structure to be observed using a benchtop microscope (JSM-7610FPlu).



**Figure II.7:** Scanning electron microscope (JSM-7610FPlu).

### **2.1.3. Thermogravimetric Analysis (TGA) :**

Thermogravimetric Analysis (TGA) is a thermal analysis technique used to determine the mass loss of a substance under controlled variations of temperature or time. This method can be used to examine the chemical, physical or physico-chemical phenomena that occur under controlled temperature conditions, and to evaluate the thermal stability of a sample. The procedure involves precise, real-time measurement of the sample's mass variation as the temperature fluctuates, usually using a sequential thermocouple in a controlled environment. TGA is usually combined with differential thermal analysis (DTA).[14]

#### **2.1.3.1. Principle**

Thermogravimetric analysis is based on the mass changes of a material subjected to either a series of temperature levels over time (constant temperature mode) or a continuous increase in heating speed. The apparatus consists of a micrometer and a heating system to measure the recorded mass gains or losses, which are analyzed by a data acquisition system. This technique allows the loss of constituent elements of materials such as polymers, oils and plasticizers to be accurately estimated, while monitoring their thermal stability.[15]

#### **2.1.3.2. Apparatus**

In this study, a type (PT 1600) thermogravimetric analyzer (TGA) was used. This device is used to measure changes in sample weight under different temperature and gas conditions.



**Figure II.8:** Typical Thermogravimetric Analyzer (PT 1600) .

#### 2.1.4. Transmission Electron Microscopy (TEM) :

Transmission Electron Microscopy is proving an invaluable tool for characterizing characterization of metal nanoparticles. The contrast visible in TEM images comes from the sample's ability to transmit or scatter electrons. Given the exceptionally high electron density of metallic nanoparticles, TEM allows us to obtain images of remarkable quality. What's more, this method makes it possible to direct observation of sample morphology at the nanometric scale.[16]

##### 2.1.4.1. Principle

The electron microscope uses an electron beam emitted by an electron gun heated to extremely high temperatures. This beam passes through a sample, producing an image on a screen connected to a CCD camera. For colloidal samples, a small drop of solution is deposited on a copper grid covered with a carbon film. The TEM operates in image mode, where electrons absorbed by the sample allow its density to be visualized, or in diffraction mode, similar to X-ray diffraction.[16]

##### 2.1.4.2. Apparatus

In this study, we used the high-resolution electron microscope HT7700, which uses Hitachi's unique 120 kV double-slit objective technology. This technology is particularly well suited to imaging high-resolution optical elements, because the low voltage improves contrast and minimizes damage. Exceptional images even at voltages as low as 40 kV. The device offers fully digitized images, with a wide range of integrated CCD camera systems. The high-sensitivity digital CCD camera enables all microscope operations via the graphical interface, including initialization alignment, adjustment and image acquisition.



**Figure II.9:** HT7700 transmission electron microscope.

## 2.2.Spectrometric analysis :

### 2.2.1.Fourier transform infrared spectroscopy (FTIR) :

FT-IR stands for "Fourier Transform Infrared", the preferred method of infrared spectroscopy. In this technique, infrared rays are passed through a sample. Some of these rays are absorbed by the sample, while the rest are transmitted unchanged. The resulting spectrum represents molecular absorption and transmission providing a unique molecular fingerprint of the sample. Like a fingerprint, no two identical molecular structures produce the same infrared spectrum, making this technique invaluable for a variety of analyses.[17]

#### 2.2.1.1. Principle

In FT-IR technology, a beam splitter is used to divide the inner infrared beam into two optical beams. One beam is reflected by a fixed plane mirror, while the other is reflected by a moving plane mirror. The distance covered by the latter varies with the movement of the mirror, resulting in interference between the two beams, generating a signal known as an interferogram. [18]

The regions of the infrared spectrum are generally divided into three categories: near infrared (400-10  $\text{cm}^{-1}$ ), mid infrared (4000-400  $\text{cm}^{-1}$ ), and far infrared (14,000-4000  $\text{cm}^{-1}$ ) Infrared photons enable chemical bonds to vibrate at specific frequencies leading to absorption of radiation at specific frequencies. [18]

When chemical bonds are exposed to infrared radiation, they absorb at frequencies corresponding to their modes of vibration, producing a spectrum used to identify functional groups and compounds. Certain impurities exhibit distinct frequencies in the infrared region, and spectral measurements of these bands are used to determine impurity concentrations and their binding to the host material. To interpret these interference signals, the Fourier transform is used to decode the individual frequencies. This transformation is performed by a computer, which then presents the desired spectral information for analysis. [18]

#### 2.2.1.2. Apparatus

In this study, a "Fourier Transform Spectrometer" was used. The device directs infrared radiation at the sample and measures the wavelengths absorbed by the substance and the intensity of this absorption. The spectra obtained were recorded using an FT/IR-4600 spectrophotometer.



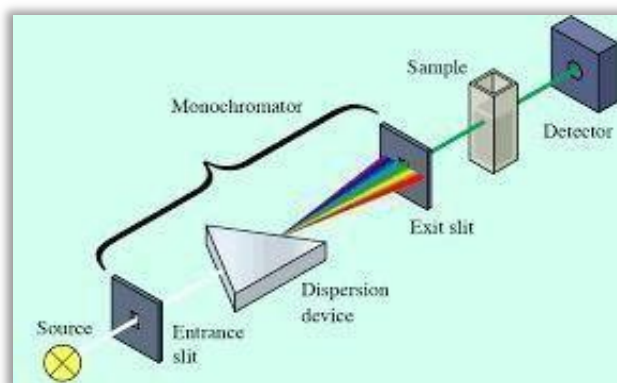
**Figure II.10:** Fourier transform infrared spectroscopy apparatus (FT/IR-4600).

### 2.2.2. Ultraviolet-visible (UV) spectroscopy :

UV-Vis spectroscopy is based on transitions between electronic energy states. Molecules can occupy several vibrational levels, separated by small energy differences. As a result, these molecules exhibit the same electronic transition, and synchronized variations in vibrational and rotational states result in energy absorption, producing spectral lines. These phenomena lead to the formation of molecule-specific absorption bands.[19]

#### 2.2.2.1. Principle

This spectroscopic device uses two light sources: a deuterium lamp for ultraviolet rays for ultraviolet rays between 200 and 340 nanometers, and a tungsten lamp for the visible for the visible region between 340 and 900 nanometers. The monochromator is used to separate the polychromatic radiation emitted by the source and adjust the wavelength of this radiation by rotating the diffraction grating. The beam leaving the monochromator is split into two beams of equal intensity: the first serves as a reference ( $I_0$ ) and the second passes through the sample ( $I$ ). The detector, known as the photomultiplier, converts the light signal into an electrical signal, which is then processed by the computer via Cary Software. The resulting UV-visible spectrum displays the absorbance value ( $\log I_0/I$ ) as a function of the wavelength used in this process, which ranges between 200 and 900 nanometers.[20]



**Figure II.11:** Schematic diagram of a UV-Visible single-beam spectrometer

#### 2.2.2.2. Apparatus

The apparatus used to measure ultraviolet rays, also known as UV spectrophotometer, is used to measure the degree of absorption and transmittance of ultraviolet light by a substance of the type (SEcomam, UViline - 9600 ) This device registers variations in light intensity in order to determine the concentration or presence of specific substances in the sample.



**Figure II.12:** Ultraviolet-visible spectroscopy instrument (SEcomam, UViline - 9600).

### 3. General information on colorants :

In our colourful world, everything is imbued with color, from the food we eat, the cosmetics we use, the clothes we wear, even the medicines we take, and much more., besides. When it comes dyes, the growing use of synthetic dyes is due to their ease of manufacture, great diversity and speed of color production. As a result, synthetic dyes have become a real and vital part of the modern chemical industry. Worldwide production of these dyes is estimated at around 800,000 tonnes per year. [21]

#### 3.1. Definition of a colorant :

A colorant is a substance with the ability to self-colour and bind to a support. The color of different substances is influenced by their chemical composition. Dyes can be divided into two main categories: those produced by chemical synthesis processes and natural dyes "obtained from mineral or organic materials ".[21]

#### 3.2. Colorant classification :

There are different types of dyes which can be classified according to their use chemical group, or their properties.[22]

##### 3.2.1. Chemical classification :

The classification of dyes according to their chemical structure is based on the nature of the chromophore group, where the distinction is made according to the type of chromophore group.[22]

**3.2.1.1. Azo dyes :**

Azo dyes are characterized by the presence of an azo group ( $-N=N-$ ) within the molecule, linking two identical or different alkyl or aryl groups. These dyes can be classified according to the number of azo chromophore groups present in the molecule, into mono-azo, diazo and polyazo. (figure II.13 (a)). [22]

**3.2.1.2. Anthraquinone dyes :**

Anthraquinone is a derivative of anthracene. It occurs naturally in certain plants. The basic molecule in this group of dyes is anthraquinone, which features the carbonyl chromophore group ( $>C=O$ ) on an ionic nucleus. (figure II.13 (b)) [22]

**3.2.1.3. Indigoid dyes :**

Indigo dyes take their name from indigo. Thus, the selenic, sulfurous and oxygenated counterparts of indigo blue produce significant hypochromic effects, with colors ranging from orange to turquoise (figure II.13 (c)). [22]

**3.2.1.4. Xanthene dyes :**

Xanthenes are tricyclic organic compounds. They consist of a pyran ring framed by two benzene rings. These dyes exhibit intense fluorescence. (figure II.13 (d)) [22]

**3.2.1.5. Triphenylmethane dyes :**

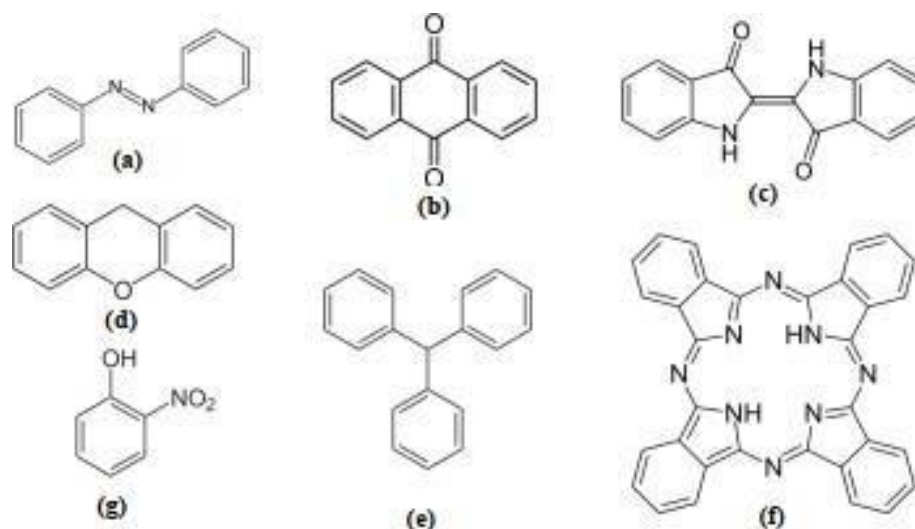
Triphenylmethanes are derivatives of methane, in which the hydrogen atoms are replaced by phenyl groups linked to a central carbon. The triphenylmethane and its homologues are the fundamental hydrocarbons from which (figure II.13 (e)) [22]

**3.2.1.6. Phthalocyanines :**

Phthalocyanines have a complex structure with a central metal atom. They are obtained by reacting dicyanobenzene in the presence of a metal halide. (figure II.13 (f)). [22]

**3.2.1.7. Nitro and nitrosated dyes :**

Nitro and nitrosated dyes are distinguished by their simple structure, characterized by the presence of a nitro group ( $-NO_2$ ) in the ortho position to an electron-donating group. (figure II.13 (g)). [22]

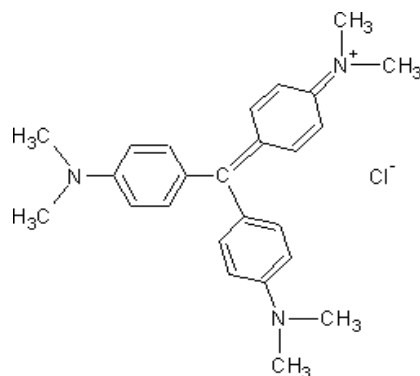


**Figure II.13:** Chemical structure of dyes: (a) azo, (b) anthraquinone, (c) indigoid, (d) xanthene, (e) triphenylmethane indigoids, (f) phthalocyanines, (g) nitrosates.[23]

### 3.2.2. Dye classification :

#### 3.2.2.1. Basic or cationic dyes :

Basic or cationic dyes are salts of organic amines, which gives them good solubility in water. Bonds are formed between the cationic sites of the dyes and the anionic sites. This type of dye is used to dye fibers containing acid groups, such as acrylic synthetic fibers. Basic dyes belong to categories such as triphenylmethanes, anthraquinones and azo dyes.[24]



**Figure II.14:** Example: crystal violet.

#### 3.2.2.2. Acid or anionic dyes :

Acid or anionic dyes are highly soluble in water thanks to the presence of sulphonate or carboxylate groups in their structure. The presence of sulfonate or carboxylate groups in their structure. These dyes belong to two main categories of chemical dyes: azo dyes and anthraquinone dyes. They are used to dye wool and silk at a temperature of °100C from acid solutions, producing vivid, long-lasting colors. These dyes also show good reactivity with certain synthetic textiles such as polyamides.[24]

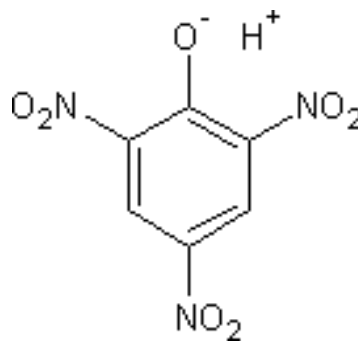


Figure II.15: Example: is picric acid.

## 4. Antibacterial activity :

### 4.1. Definition of bacteria :

Bacteria are single-cell micro-organisms found in a variety of environments, including extreme conditions. They live in colonies of millions of cells. A bacterial cell is simple, without a cell nucleus, containing only a membrane and a few organelles. They are classified as prokaryotes because they have no nucleus. The cell contains DNA and ribosomes for protein synthesis. Some bacteria are useful, others cause disease, underlining their importance to human life and the ecosystem.[25][26]

### 4.2. Types of bacteria :

Gram staining is a crucial technique for identifying bacterial strains. It guides the selection of tests and culture media. Gram-negative bacteria appear pink, while Gram-positive ones are blue or purple, revealing differences in their cell wall. This method also assesses the resistance of strains to alcohol. Bacteria vary in shape, size and function, with thousands of different types.[27]

#### 4.2.1. Gram-negative bacteria (-):

##### 4.2.1.1. Escherichia coli :

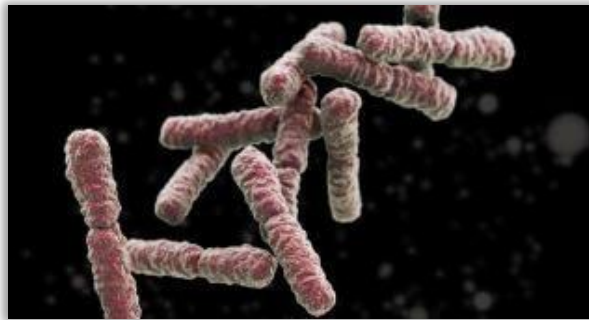
a Gram-negative bacillus, is part of the normal microflora of man and warm-blooded animals, including mammals and birds. This bacterium is used as a standard reference in research due to its low pathogenicity and ease of handling. easy to handle. It reproduces rapidly, with a division cycle of around 20 minutes in the laboratory 3to 5 hours in vivo under ideal growth conditions. The slower growth rate observed in vivo is attributed to a prolonged lag phase influenced by the availability of nutrients in its environment.[28]

##### • Habitat

Escherichia coli is a commensal bacterium commonly found in the digestive tract of humans and many animal species. It makes up a significant of the aerobic bacterial population of the intestinal flora, with around  $10^8$  colonies per gram of faeces, contributing to an overall bacterial count of  $10^{10}$  to  $10^{12}$  bacteria per gram. [28]

- **Morphology**

These are Gram-negative bacilli, which may be motile or immobile, sometimes immobile, sometimes capsulated. Typically, they appear as rods 2-4  $\mu\text{m}$  in length.[28]



**Figure II.16:** Escherichia coli .[29]

#### 4.2.1.2. Pseudomonas aeruginosa :

Pseudomonas bacteria are aerobic, mobile, pigmented organisms, naturally resistant to many antibiotics and often found in aquatic environments. They are known to contaminate medical products and are associated with hospital-acquired infections, often being resistant to several antibiotics, which complicates their treatment. Among them, Pseudomonas aeruginosa is particularly formidable in environments where immune defenses are compromised.[28]

- **Habitat**

The pyocyanin bacillus can live freely in natural wetlands in the digestive tracts of humans and animals.[28]

- **Morphology**

Pyocyanin is a Gram-negative, highly motile, monotrich bacillus sometimes surrounded by a peribacillary mucous substance. [28]



**Figure II.17:** Pseudomonas aeruginosa. [29]

#### 4.2.2. Gram-positive bacteria )+( :

##### 4.2.2.1. Staphylococcus aureus :

Staphylococcus aureus is a Gram-positive cocci bacterium known for its pyogenic and toxigenic nature, contributing to a variety of community and hospital infections, which poses a major public health problem. It causes suppurative infections resulting from bacterial

multiplication, and toxigenic infections induced by specific toxins. When it penetrates the body, it can cause a whole range of infections including boils, carbuncles, pneumonia and bacteremia.[29]

- **Habitat**

*Staphylococcus aureus* is a commensal of the skin and mucous membranes of humans and animals (rhino-pharynx, intestine). It is found on the nasal mucosa of around a third of normal subjects. Eliminated in the external environment, this bacterium can survive for long periods in the environment.[29]

- **Morphology**

*Staphylococcus aureus* appears as isolated Gram-positive cocci isolated, in diplococci or grouped in polyhedral clusters evoking the appearance of a bunch of grapes.



**Figure II.18:** *Staphylococcus aureus*. [29]

#### 4.2.2.2. *Bacillus subtilis* :

*Bacillus subtilis* is a Gram-positive bacterium, common in soils and mobile, It is strictly aerobic and catalase-positive. It forms highly resistant spores in the environment and can also form biofilms. Although it is generally non-pathogenic to humans, except in rare cases of food poisoning, it is sometimes used to help intestinal microbiota. Its genome has been fully sequenced and used in the laboratory to study various metabolic pathways, cellular cell differentiation and gene regulation. It is also an important source of enzymes for the food and pharmaceutical industries.[30]

- **Habitat**

*Bacillus* are bacteria found mainly in the soil, where they contribute to the carbon and nitrogen cycles. Their ability to form resistant spores and adopt various vegetative forms enables them to survive in a variety of environments, including freshwater, seawater and food. They can also contaminate laboratory cultures if protocols are not rigorously followed.[30]

- **Morphology**

*Bacillus* are large, rectangular bacteria with square or rounded ends. They range in size from 0.5x1.2  $\mu\text{m}$  to 2.5x10  $\mu\text{m}$ . These bacteria can form spores and are generally

Gram-positive, although this may vary in very young cultures. They are generally mobile thanks to their peritriche ciliature, although some species are immobile. Bacillus can be strict or facultative aerobes, producing free spores or endospores. Some species, such as *Bacillus anthracis* and *Bacillus megaterium*, may also have a capsule.[30]



**Figure II.19:** *Bacillus Subtilis*.

## 5. Mining waste :

Mining is the extraction of mineral substances from the earth for profit. including metals such as iron and copper, non-metallic minerals such as sand and gravel such as sand and gravel, and fossil fuels such as coal. This process generates various types of waste, including waste rock, selective waste rock and tailings from all of which present environmental risks. Proper is essential to preserve the environment and prevent contamination of the biotope. Mining waste includes materials resulting from the exploration, mining and processing of minerals, including natural materials such as waste rock and gangue, and man-made materials such as tailings and rejects from concentrators.[11]

## 6. Geology of Djebel Onk :

### 6.1. History of geological research at Djebel Onk :

Algerian phosphates were first discovered at BOUGARI by PH. THOMAS in 1873, shortly before the Gafsa phosphates in 1855. The Djebel Onk deposit was by JOLEAU in 1906-1907, where two phosphate layers were found in the Oued de Djibouti ravine. in the Oued de Djemi-Djema ravine south of Djebel Onk. In 1912, DESSERT provided the first information on Algerian phosphate deposits, particularly in the Djebel Onk region, with Djebel Onk region, with detailed lithological sections. Geological knowledge progressed thanks to studies by R. LAFFITTE (1939), L. Cayeux (1939-41-50) and R. FLANDRIN (1948). [32]

In 1951, L.VISSE detailed the stratigraphy and estimated reserves of the Djebel Djemi - Djema phosphate deposit. From the 1960 s, driven by the industrialization of Algeria, phosphate exploitation became a priority. Airborne radiometric prospecting trials were carried out from 1961 to 1963, following the methods successfully used in the Tellian Atlas.

RANCHIN (1963) drew up geological maps on a scale of 1:5000. SONAREM relaunched research and prospecting phosphate prospecting in eastern Algeria from 1971 to 1974, based on aero-radiometric surveys.

From 1985 to 1987, E.N. FERPHOS commissioned EREM to evaluate the phosphate resources in the Djebel Onk region, which led to an extensive drilling program totalling 10,732 metres of core samples. [33]

In April 1992, a contract was signed between EN FERPHOS and the consultant BRGM/SOFREMINEs for the compilation of technical and economic elements to draw up a development project for the Djebel Onk phosphate deposits. deposits at Djebel Onk. In 1993, BRGM provided a geological expertise report on all the deposits at Djebel Onk. [34]

## 6.2. Geographical location :

The Djebel Onk region is located in southeastern Algeria, around 100 km from the Wilaya of Tébessa and 20 km from the Algerian-Tunisian border, on the road linking Tébessa to El Oued. It represents the natural boundary between the high plateaux of Constantine and the Saharan domain. The Djebel Onk massif, culminating at 1198 m at Djebel Tarfaya, is a limestone 20km long. This region, situated in the extreme NNE of Algeria bounded to the north by the wilaya of Souk-Ahras, to the south by the wilaya of El Oued, and to the west by the wilayas of Khenchela and Oum El Bouaghi. The lowest altitudes at the foot of Djebel Onk are around 635 m .[15]

• The Djebel Onk phosphate massif comprises five deposits: Djemi-Djema, Kef Essenoun, Djebel Onk Nord, Oued Bétita and Bled El Hadba .[15]

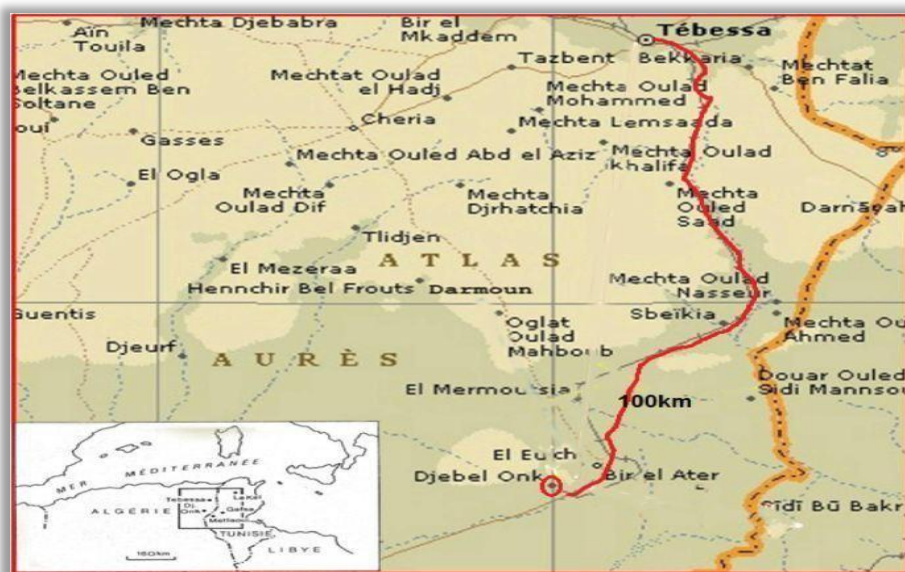


Figure III.20: Geographical location map of Djebel Onk .

### 6.3. Phosphate ore processing methods:

#### 6.3.1. Mechanical preparation:

Prior to the actual processing, the ore undergoes an initial treatment designed to prepare it for subsequent processing stages. This treatment comprises several processes:[32]

**a) Crushing :** The aim is to reduce the block size from 1000 mm to a maximum of 200 mm using a "BABITLESS" gyratory cone crusher and a hammer mill (HAZEMAG) equipped with a scalping system.

**b) Grinding:** After the initial process, the ground product is further reduced to 20 mm with a reduction ratio of ten (10) using three articulated hammer mills (WEDAG). The product is then fed to the screening plant.

**c) Screening:** The screening process uses three vibrating screens (WEDAG) to eliminate products larger than 15 mm, with a weight efficiency of 95%. Two inclined vibrating screens (HAZEMAG) are used for Kef Essnoun materials. The screen rejects are recycled, while the WEDAG screen rejects are sent to slag heaps. The main objective is to obtain a product with a size of less than 15 mm to facilitate processing on the production lines.

#### 6.3.2. Wet processing (de-sludging) :

This process, carried out in the calcination workshops (DK1), recovers ore which typically contains 69% to 77% tricalcium and 73% to 77% TPL, according to BRGM. The process comprises several stages:[36]

**a) De-sludging :** The purpose of this processing step is to purify the ore by removing impurities such as clays, silicates, organic matter and salts. It comprises several stages, including pulping, wet screening, classification, hydrocycloning and filtration. The ore is pulverized with water, then passed through curved screens to remove fine particles. Hydrocyclones recover fine particles, while high-grade particles are centrifuged to obtain a final product with a TPL content of 63% to 64.5% for further processing.

**b) Washing:** This stage improves ore quality by reducing its sludge content through washing. The water used is then treated in the washing thickener to eliminate the sludge and enable it to be reused.

**c) Drying:** The sludge by-product is a semi-finished product that must be dried to a moisture content of 1% before it can be marketed: kiln drying and horizontal kiln drying.

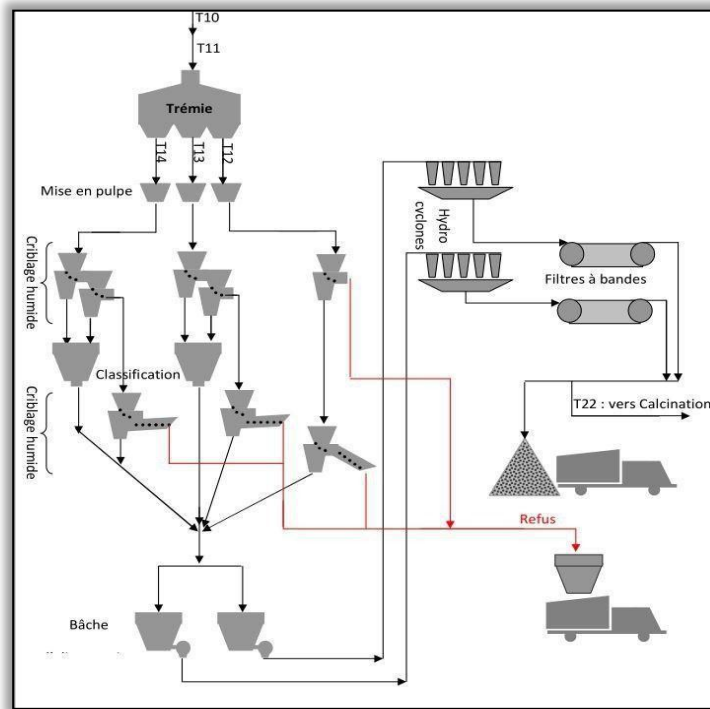


Figure III.21: De-sludging technology diagram. [36]

### 6.3.3. Dry treatment (dedusting) :

The purpose of the dust removal process is to enrich phosphate ore physically and mechanically to obtain an average concentrate containing 29 to 26.75%  $P_2O_5$  and 12.6% MgO.[17] The objective is to transform an initial ore of 54 to 56% DWT into a commercial product of 62.5 to 63.5% DWT, with particle sizes ranging from  $800 \mu$  to  $90 \mu$ . Each processing line has a capacity of 230 T/h in feed and 137.5 T/h in discharge, with a yield of 60 to 62% by weight. The process comprises five dry preparation and enrichment stages.[36]

a) **Fluidized-bed drying:** This process removes certain finer solids by entraining them in fluidizing gases. by entraining them in fluidizing gases. It comprises two drying furnaces with two types of behavior combustion and dilution, and fluidized-bed drying.

b) **2 mm screening:** Eliminates products larger than 2 mm using screens equipped with a 2 mm sieve, thus rejecting coarse materials larger than 2 mm (limestone). Materials smaller than 2 mm are accepted and sent to crushers(88 % efficiency).

c) **Attrition milling:** Releases part of the exogenous phosphate grains to enable better final enrichment by granulometric separation, using DRAGAN" mills equipped with rotor, hammers and grinding chamber.

d) **Turbo-ventilated selection :** Aims to enrich the product by eliminating fines below 00microns using fans.

e) **0.8 mm screening :** Follows the same principle as 2 mm screens, but eliminates phosphate grains phosphate grains larger than 0.8 mm.

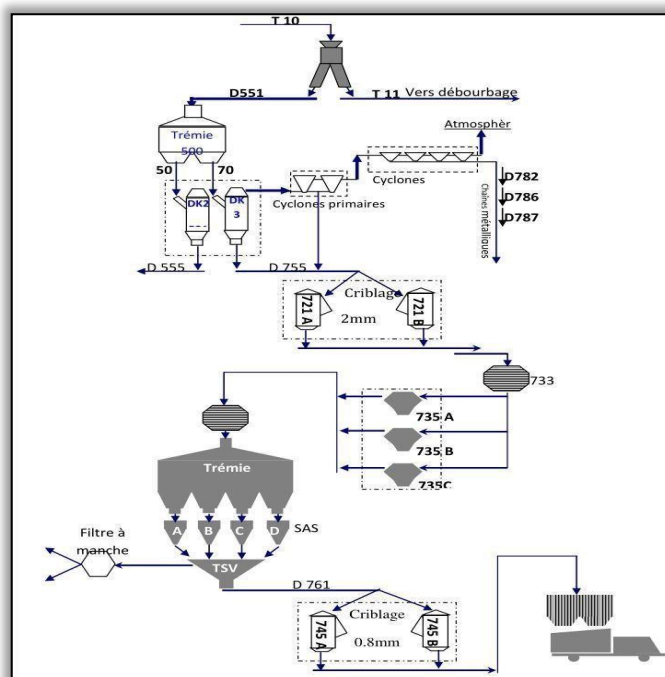


Figure III.22: Technology diagram for dust removal. [36]

## 7. Study of the mint plant :

### 7.1. General information on medicinal and aromatic plants :

Medicinal and aromatic plants are an essential source of medicines, which are found in nature and contain active substances with physiological effects and medical uses. These active substances include extracts of medicinal plants, as well as the essential oils present in some of them some of them, such as mint .[38]

### 7.2. Classification of medicinal and aromatic plants : [39]

- Classification of plants according to the active principle they contain.
- Commercial classification of medicinal plants according to their uses.
- Chemical classification of plants.
- Classification of plants according to the presence of the active principle.

### 7.3. Mint :

The Mint genus of the Lamiaceae family comprises 18 species and 11 hybrids, characterized by high morphological variability and frequent hybridization. These plants, such as *Mentha spicata*, *Mentha x piperita*, *Mentha pulegium* and *Mentha aquatica*, have been used since Antiquity in food, medicine and cosmetics for their aromatic properties. Their essential oils, rich in compounds such as menthol, carvone and menthone, vary according to plant type, growing conditions and extraction method. Although the Mint genus originated in Europe and Asia, it is now widespread throughout the world.[40]



**Figure III.23:** Map of geographical distribution of mint .

### 7.3.1. Botanical classification of mint :[41]

<i>Kingdom</i>	<i>Plantae</i>
<i>Division</i>	<i>Embryophyta</i>
<i>Class</i>	<i>Magnoliopsida</i>
<i>Order</i>	<i>Lamiales</i>
<i>Family</i>	<i>Lamiaceae</i>
<i>Genus</i>	<i>Mentha</i>
<i>Species</i>	<i>Mentha xpiperita</i>
<i>Scientific name</i>	<i>Mentha xpiperita</i>

**Table III.1:** Botanical classification of mint. [41]

### 7.3.2. Morphological description of spearmint :

Spearmint is an herbaceous perennial that can grow up to a meter in height, with a quadrangular stem and light-green, toothed leaves. Its violet, pink or white flowers are arranged in terminal spikes without bracts. Mint is easy to grow, spreads quickly and requires frequent watering, especially in summer. It was widely used in ancient times by the Egyptians and Greeks as a popular beverage, and its cradle of origin lies in the Mediterranean basin region.[42]

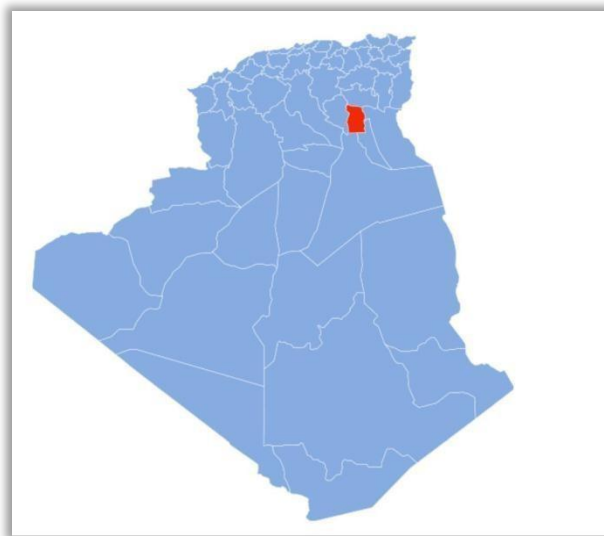
### 7.3.3. Chemical composition of mint :

Mint is considered an important plant due to its wealth of medicinally active medically active components. It contains essential oils in concentrations of between 0.8% and 2.5%. It also contains carvone at a level of %55It also includes flavonoid compounds such as thymonine, caffeic acid derivatives esters and terpenoids. The essential components of mint menthol and limonene. It is rich in vitamins, notably B and A, and high in minerals such as calcium, magnesium, sulfur, potassium, sodium and iron.

Spearmint leaves contain between 45% and 60% carvone, between 4% and %20 menthones, and between 4% and 20% esters. The spicata type of mint is rich in monoterpenes such as carvone, limonene, menthone and menthol, It has also been reported that mint oil from the spicata type of the mint family contains 29% carvone, 14% trans-carvone, 3.2% carvacrol and 0.4% linalool.[43]

### 7.3.4. Parts used in the experiment :

In this work, we used parts of the mint plant: Stem and Leaves. The sample was collected in December 2023 in an agricultural area called El- Barkajiya, located about 25 km west of the Wilaya El-Meghaier, which is characterized by the fertility of its soil and its suitability for all types of agriculture.



**Figure III.11:** Location map of Wilaya El-Meghaier .

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# **Chapter III: Synthesis, Results and Discussions**

### III.1. INTRODUCTION:

The synthesis of nanocomposite is usually done using various physical and chemical processes such as vapor deposition, aerosolization, photochemical reduction, etc. The chemicals used in these syntheses are often toxic, expensive, and unresponsive to the environment. The aim of this chapter is to present the synthesis of HD NC from metal waste by green chemistry (mint plant extract). In this context, we seek to develop new simple and reproducible synthesis strategies using as few non-toxic chemicals as possible, to minimize reaction by-products and residual ions that may hinder the fundamental properties of the final material .

The prepared of HD NC are characterized using ultraviolet-visible spectrum, X-ray diffraction, and Fourier transform infrared spectrum FTIR.

### III.2. MATERIALS AND METHODS:

#### III.2.1. Plant material :

- Mint plant.



Figure III.1: Mint plant

#### III.2.2. Chemical products :

- Mining waste
- Distilled water
- Sodium hydroxide (NaOH)

#### III.2.3. Characterization :

- IR absorption spectroscopy (FTIR)
- X-ray diffraction (XRD)

#### III.2.4. Application :

- UV-visible spectroscopy
- Anti-bacterial activity

#### III.2.5 Synthesis of HD NC by mint extract :

Mint plant extract is prepared in the following way: After collecting the sample, we weigh 500 g and wash it carefully to remove impurities. Drying is done on dry and ventilated

ground to preserve the therapeutic properties. After drying, the plant is weighed and stored in a paper box. A sample of dried mint 100 g is immersed in 1 liters of distilled water for 24 hours at 25°C. After extraction, the extract is filtered twice to remove impurities and stored in a clean glass jar in a dry, cool, and dark place to maintain its quality. We prepared 10 g of metal waste, then poured 1 liter of the plant extract we prepared earlier and heated the mixture for 1 hour, stirring occasionally. After half an hour, we added 2.5 ml of sodium hydroxide to speed up the reaction. When the mixture reached a temperature of 75°C, we maintained this temperature for another hour, during which time the mixture turned dark brown in color, indicating the formation of nanoparticles. We let the mixture cool away from light. We concentrated the sediment using centrifugation at 30,000 rpm for 3 minutes, then washed the sediment three times with distilled water and returned it to the centrifuge until the material settled to the bottom. After filtration, we dried the sediment at 75°C overnight. We then ground it to a fine powder weighing 7.1 g, placed it in a calcination oven at 500 °C for 4 hours, and after calcination we weighed it and found 6.7 g of the final compound.[1]

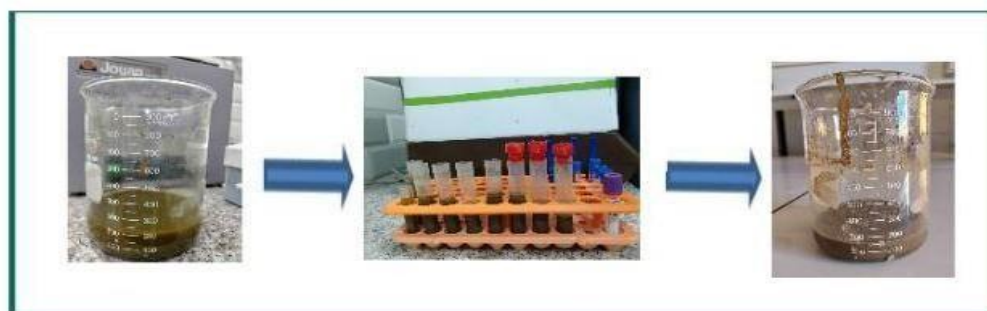
**Scheme of the experiment**



Step 1: Plant extract preparation .



step 2: Nanocomposite synthesis .



step 3:Washing and Separation Phase (Centrifuge).



**HD - Nanocomposite**

Figure III.2: HD NC synthesis protocol.

### III.3. RESULTS AND DISCUSSION :

#### III.3.1. X-ray diffraction analysis :

In (Figure III.3) the X-ray diffraction (XRD) pattern of the synthesized HD nanocomposite (NC) showed several peaks. The broad nature of these peaks suggests that the material produced is composed of nanoscale particles. XRD analysis revealed distinctive diffraction peaks at angles of  $31.779^\circ$ ,  $34.430^\circ$ ,  $36.265^\circ$ ,  $47.554^\circ$ ,  $56.615^\circ$ ,  $62.876^\circ$  and  $72.587^\circ$ , corresponding to the (0 0 2), (0 2), (1 1 0), (1 0 3) and (0 0 4) crystal planes, respectively. These peaks are characteristic of ZnO nanoparticles, indicating their hexagonal crystal structure in accordance with the standard ZnO nanoparticle pattern [2]. Furthermore, the presence of CuO nanoparticles was confirmed through the XRD spectrum, which showed peaks at  $2\theta = 38.941^\circ$ ,  $48.743^\circ$ ,  $61.582^\circ$ ,  $66.276^\circ$ ,  $68.120^\circ$  and  $75.262^\circ$ , corresponding to the (200), (-202), (-1 1 3), (-3 1 1), (2 2 0) and (-222) crystal planes, respectively. These peaks are consistent with the monoclinic crystal structure of CuO nanoparticles. In addition, the XRD pattern showed distinctive peaks at  $32.244^\circ$ ,  $36.041^\circ$ ,  $54.195^\circ$  and  $58.552^\circ$ , corresponding to the (701), (011), (011) and (011) crystal planes, respectively. These peaks are consistent with the cubic structure of  $\text{Cu}_2\text{MgO}_3$ , providing strong evidence for the formation of the HD NC.

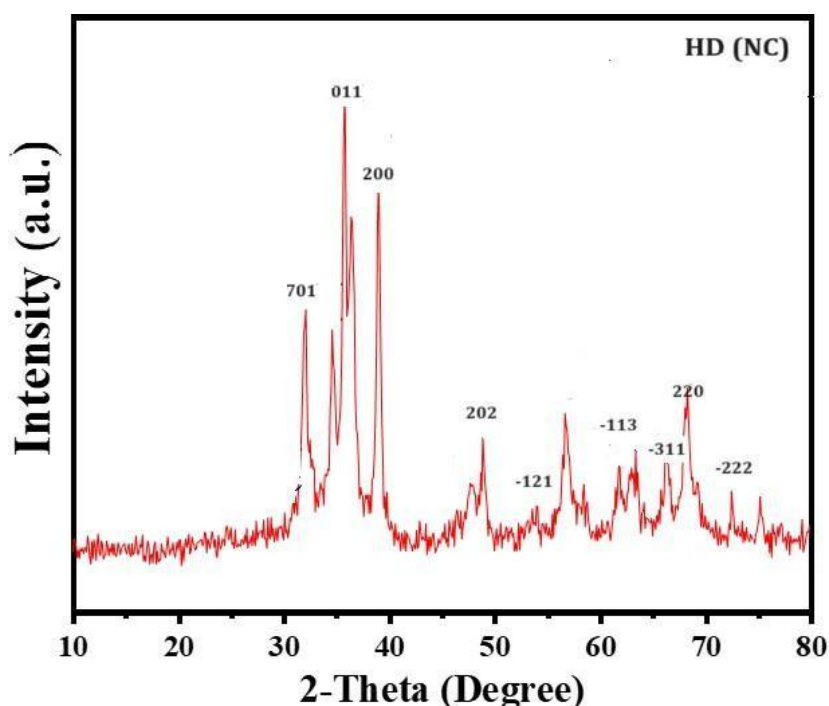
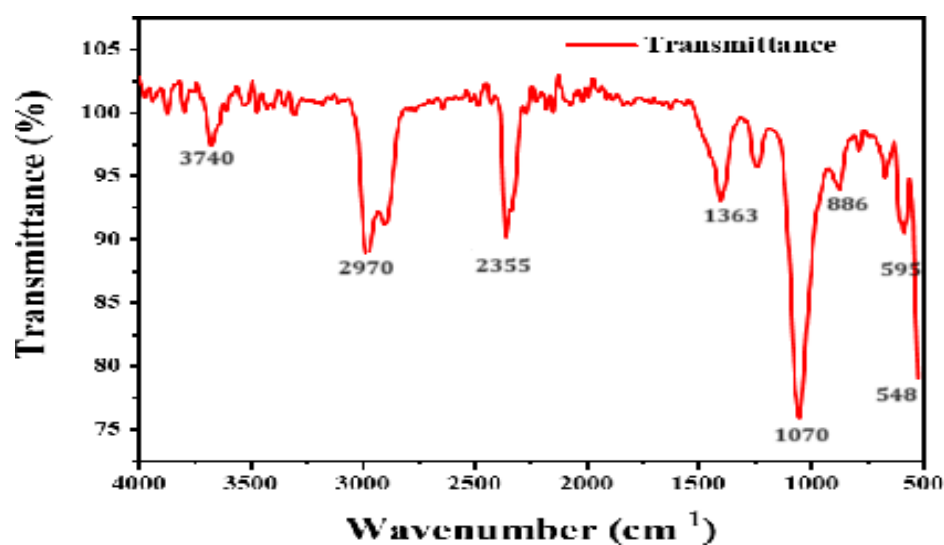


Figure III.3: XRD patterns for the synthesis of HD NC .

### III.3.2. FTIR infrared spectroscopy :

FTIR analysis reveals important information about the chemical composition and bonding in the synthesized HD nanocomposites (**Figure III.4**). Several characteristic peaks were observed, suggesting the presence of specific functional groups and chemical bonds. The broad peak at  $3745\text{ cm}^{-1}$  probably indicates the presence of hydroxyl (-OH) groups [3], possibly originating from the mint leaf extract used in the biosynthesis process. The peak at  $1078\text{ cm}^{-1}$ , due to C-C stretching in the region of lower wavenumbers, such as  $865\text{ cm}^{-1}$ ,  $595\text{ cm}^{-1}$  and  $548\text{ cm}^{-1}$ , are suggestive of  $\text{Cu}_2\text{MgO}_3$ , ZnO and CuO vibrations, respectively [4-8], implying the formation of metal oxides within the nanocomposite (HD NC). The distinct wavenumbers observed in the FTIR spectrum provide valuable information on the chemical composition and bonding within the nanocomposite, indicating the coexistence of organic and inorganic components, such as metal oxides, resulting from the biosynthesis process.

Due to the presence of these functional groups within the antioxidant polyphenol structure, the spectrum can demonstrate the presence of phenolic compounds in the plant extract.

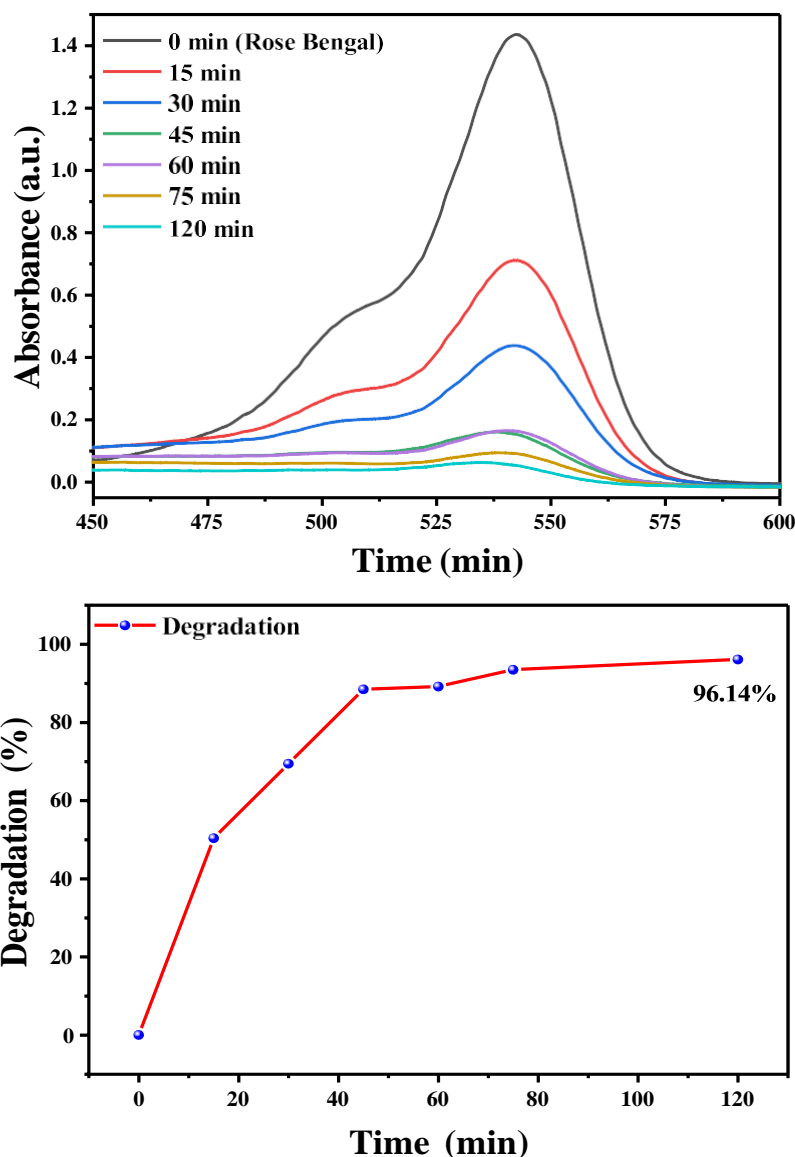


**Figure III.4:** FTIR spectrum of synthesized HD NC.

### III.3.3. Photocatalytic degradation efficiency :

The study focused on the photodegradation of Rose Bengal (RB) using HD NC under solar irradiation at different time intervals (15, 30, 45, 60 and 120 minutes). Rose Bengal was chosen as a model organic dye because of its relevance to many dyes commonly found in wastewater [9] UV-vis absorption spectra showed a progressive reduction in peak intensity at the start of the experiment, indicative of the gradual decomposition of RB molecules. More specifically, it was observed that a substantial proportion of the RB dyes had undergone degradation after 45 minutes of exposure to solar irradiation (**Figure III.5**). The sudden drop observed after 15 minutes can be attributed to the dynamic interplay between various factors

affecting the photocatalytic degradation process. One possible explanation is the adsorption equilibrium initially established between the RB dye and the nanocomposite surface. During the initial stages of the photocatalytic reaction, the active sites on the HD NC surface rapidly adsorb RB molecules, leading to a significant reduction in the RB concentration in the solution. As the reaction progresses, saturation of these active sites could slow the adsorption rate, subsequently affecting the observed degradation kinetics. In addition, the formation of intermediate species during the degradation process could also influence the rate of RB degradation, leading to the observed fluctuation in removal efficiency. To assess the elimination mechanisms contributing to the observed degradation, the experiment was extended to 120 minutes under direct sunlight conditions, highlight the role of the adsorption pathway. Extending the experiment to 120 minutes demonstrated an impressive 96.14% removal efficiency by adsorption.



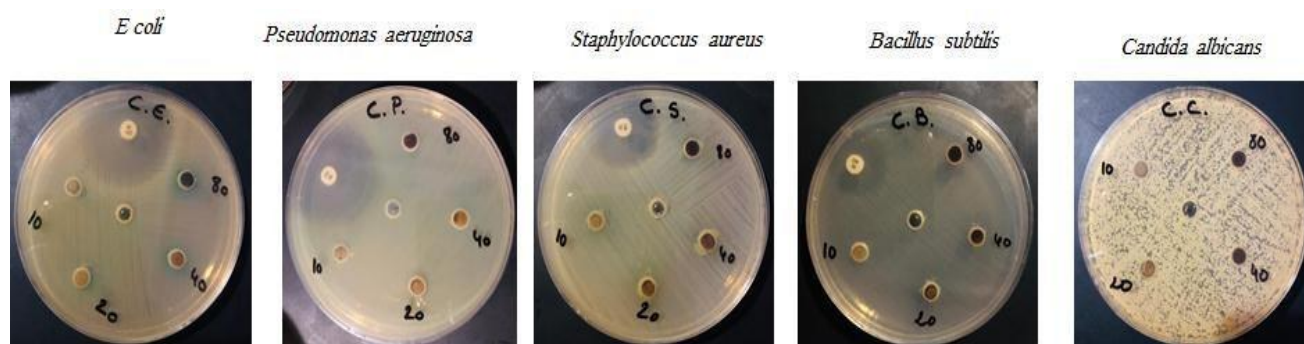
**Figure III.5:** Time effect reaction of HD NC on photodegradation of RB dye.

### III.3.4. Assessing the antibacterial activity of HD NC :

Agar Diffusion Method (Well Method) This is the basic technique used to study the antimicrobial effect of a substance. Petri dishes containing Sabouraud dextrose agar supplemented with 2% glucose (for yeasts) and Mueller-Hinton agar (for bacteria) are aseptically inoculated with a suspension of  $10^6$  cells/mL obtained from a young culture of yeasts or bacteria, respectively. Inoculation is done by swabbing. After the dishes have dried, the agar is perforated at the center using the upper part of a Pasteur pipette. The resulting cavities are filled with the aqueous solution of the extract at concentrations of (20, 40, 100 and 10 mg/mL) (approximately 50  $\mu$ L per well). The dishes are incubated in an incubator at 37°C for 48 hours for yeasts and 24 hours for bacteria. Inhibitory action is indicated by the formation of a zone of inhibition around the wells. The results are read by measuring the diameters of the inhibition zones. A product is considered active if the diameter of the inhibition zone is greater than 6mm.[10][11]



**Figure III.6:** Anti-microbial Tests



**Figure III.7:** Photographs of Petri dishes showing antibacterial activity.

Strains used	Microbial inhibition				
	80mg/ml	40mg/ml	20mg/ml	10mg/ml	CN
<i>Escherichia coli</i> ATCC 25922	NI	NI	NI	NI	32
<i>Pseudomonas aeruginosa</i> ATCC 27853	NI	NI	NI	NI	31
<i>Staphylococcus aureus</i> ATCC 25932	NI	NI	NI	NI	25
<i>Bacillus subtilis</i> ATCC 25973	NI	NI	NI	NI	18
<i>Candida albicans</i> ATCC 10231	NI	NI	NI	NI	/

NI = No Inhibition, CN = Gentamicin (CN) 30ug Discs.

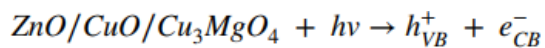
**Table III.1:** Results of antibacterial tests.

• Following this test, concentrations of the nanocomposite were tested on the growth of different types of bacteria. The results showed that the nanocomposite had no zones of antibacterial inhibition, and all the results were negative, so it cannot be considered antibacterial.

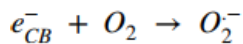
#### III.4. HD NC Formation Mechanism :

(Figure III.8) illustrates the potential mechanism of photocatalytic degradation of RB dyes using HD NC under sunlight exposure. The photocatalytic degradation mechanism can be explained as follows: When exposed to UV irradiation, electrons on the HD surface are energized. Light-generated electrons in the conduction band (BC) can react with adjacent oxygen molecules ( $O_2$ ) to produce superoxide anions ( $O_2^-$ ) [12]. Similarly, positively charged "holes" combine with hydrogen molecules in water ( $H_2O$ ) to generate hydroxyl radicals ( $OH^\cdot$ ). These superoxide anions ( $O_2^-$ ) and hydroxyl radicals ( $OH^\cdot$ ) play a crucial role in the decomposition of dye molecules [13]. They interact efficiently with the dye molecules, leading to the production of carbon dioxide and water. However, the band gap of HD and the easy recombination of charge carriers determine the photocatalytic efficiency of HD. Surface roughness and band gap have a remarkable effect on the photocatalytic efficiency of HD

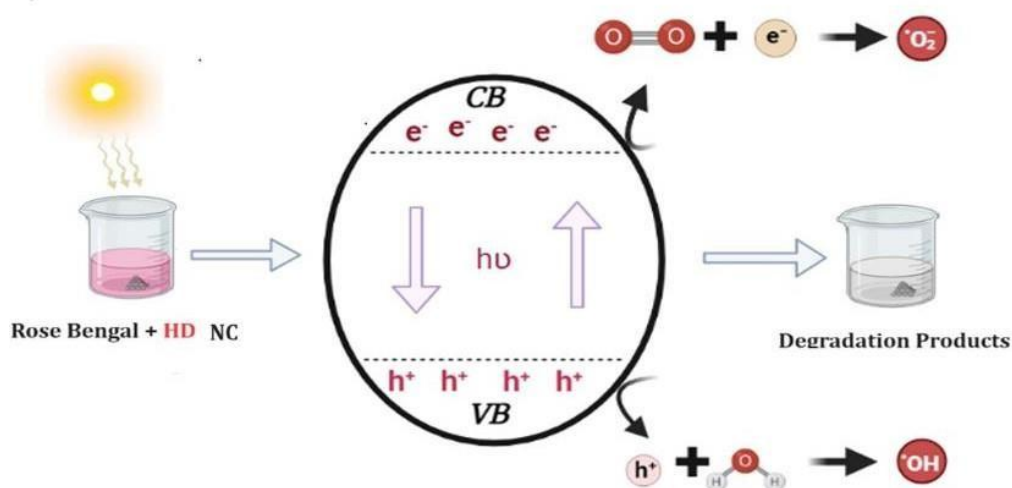
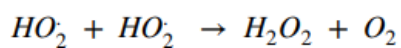
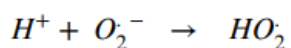
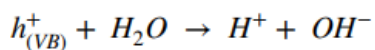
semiconductors[14]. The resulting photocatalytic reaction is represented by the following equation.



A superoxide radical anion is generated



Transformation of the  $\text{OH}^-$  group into OH through hole-mediated neutralization



**Figure III.8** :Possible mechanism of Rose Bengal dye Degradation under sunlight irradiation using HD NC.

### Conclusion :

In this work, we achieved our main Objective of preparing a nanocomposite using biosynthesis, starting from mint plant extract and replacing the synthesized metals with mining waste from the Djebel-Onk mine in Tebessa, providing a low-cost, simple and environmentally friendly method .

The prepared HD nanocomposite was characterized by X-ray diffraction, FTIR spectroscopy and UV-Visible spectroscopy and tested for its antibacterial activity.

X-ray diffraction analysis and FT-IR spectroscopy results indicate the successful nanocomposite formation

XRD revealed the presence of characteristic peaks for ZnO indicating the hexagonal crystal structure, while the peaks for CuO confirm the monoclinic crystal structure, and the peaks for Cu<sub>2</sub>MgO<sub>3</sub> show the cubic crystal structure. These results demonstrate the excellent crystalline quality and integrated morphology of HD NC .

FT-IR analysis shows the chemical composition of HD NC and the reactions present in it. The spectra showed several characteristic peaks indicating the presence of hydroxyl groups (-OH), and other peaks associated with ZnO/CuO/Cu<sub>2</sub>MgO<sub>3</sub> vibrations which confirm the formation of metal oxides within HD NC, the presence of functional groups associated with antioxidant polyphenols indicates the presence of phenolic compounds in the mint extract used in the green synthesis process. These results highlight the integration of organic and inorganic components and the overall composition in the HD NC structure, allowing its use in advanced nanoscale applications such as: Wastewater treatment and removal of organic and inorganic pollutants and effluents.

UV analysis results indicated the effectiveness of HD NC in degrading Rose Bengal dye under sunlight. It shows a gradual degradation and decrease in dye concentration over time. During the initial stages, this decrease is associated with a dynamic interaction between the RB dye and the nanocomposite surface. RB molecules are rapidly adsorbed on the active sites of HD NC, and as the reaction progresses, these sites become saturated, slowing down the rate of adsorption. With sufficient time extension (120 minutes), the results show a high removal rate of 96.14%, which enhances the effectiveness of HD NC in treating the dye under sunlight, opening new prospects for the use of the product in effective wastewater treatment.

The results of testing the effect of different concentrations of HD NC on bacterial growth: *Escherichia coli*/ *Pseudomonas aeruginosa*/ *Staphylococcus aureus*/ *Bacillus subtilis*/ *Candida albicans* , there were no zones of inhibition and all results were negative, thus HD

## *Conclusion*

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NC cannot be considered antibacterial, suggesting that additional studies should be conducted to determine its actual antibacterial potential and identify its possible mechanisms of action.

We can say that we were able to exploit renewable environmental resources, namely mint plant extract and mining waste from Djebel Onk in Tebessa, for the synthesis of nanocomposites .

Based on the results obtained in this study, we developed possible suggestions for the utilization of the HD NC product: Wastewater treatment and removal of organic and inorganic pollutants and dyes thanks to its efficiency in degrading them under sunlight .

Improving the efficiency of solar cells thanks to the product's efficiency in degrading dyes under sunlight, using HD NC to increase the conversion of light energy into electrical energy. Improving plant growth and quality and increasing agricultural production by using HD NC as a growth promoter or pest control agent, and using it in the design of water filters or air pollution treatments.

### **perspective**

These are some of the areas we have highlighted in exploiting HD NC, and there are still many more applications that need to be explored and deepened by extending this study with more analysis techniques: Transmission electron microscopy(TEM),scanning electron microscopy(SEM),Atomic force microscopy(AFM), and thermogravimetric analysis (TGA)to elucidate the shape and size of the prepared nanoparticles, as well as testing the antibacterial efficacy of HD to include other types of bacteria.

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