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Topic :

Green Synthesis and Characterization of Zinc Oxide Nanoparticles

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Major in Organic Chemistry

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Acknowledgements

Dedications

I dedicate this modest paper as a tribute to all the teachers who guided and inspired me throughout my education : ***"A good teacher is like a candle. He consumes himself to light the way for others"*** *Mustafa kemal Atatürk*

To begin with, I would like to thank my secondary and high school teachers, respectively ***Mr.Wenougi*** who introduced me to the infinite world of chemistry, and ***Ms. Boufassa*** who opened the doors of her home and her heart to me. Thank you for all your lessons and your encouragement.

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Abstract :

The main purpose of this work is the biosynthesis of zinc oxide nanoparticles with a green approach using aloe vera extracts. The process used is low-cost and environmentally friendly with no waste. The recovered ZnO powder was calcined at temperatures of 400°C and 500°C for 2h and 4h. ZnO nanoparticles were characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The XRD diffractograms revealed a zincite structure of ZnO with nanometric size. The average crystallite size is 44.5 nm. FTIR spectra confirm the presence of secondary metabolites within the extract and show the chemical groups present in the synthesized material. SEM images show ZnO nanoparticles of different shapes, such as ZnO nanosheets with well-defined particle boundaries and nanosized nanowires with particle agglomeration. The elemental composition of ZnO NPs analyzed by EDX revealed the presence of zinc, and oxygen, confirming the formation of ZnO nanoparticles and other minerals in the aqueous plant extract.

Résumé :

L'objectif principal de ce travail est la biosynthèse de nanoparticules d'oxyde de zinc avec une approche verte moyennant des extraits d'aloe vera. Le procédé utilisé est peu couteux et respéctueux de l'environement avec zero déchets. La poudre de ZnO récupérée a été calcinée à des températures de 400°C et 500°C pendant 2h et 4h. Les nanoparticules de ZnO ont été caractérisés par diffraction des rayons X (DRX), spectroscopie Infrarouge à Transformée de Fourier (FTIR), microscopie électronique à balayage (MEB) et spectroscopie de rayons X à dispersion d'énergie (EDX). Les diffractogrammes de DRX ont révélé une structure zincite du ZnO avec des tailles nanométriques. La taille moyenne des cristallites est de 44.5 nm. Les spectres FTIR confirment la présence des métabolites secondaires au sein de l'extrait et montrent les groupements chimiques présents dans le matériau synthétisés. Les images SEM montrent des nanoparticules de ZnO de différentes formes, comme des nanofeuillets de ZnO avec des limites de particules bien définies et des nanofils de taille nanométrique avec une agglomération des particules. La composition élémentaire des ZnO NPs analysée par EDX a révélé la présence de zinc, d'oxygène, ce qui confirme la formation de nanoparticules de ZnO et d'autres minéraux dans l'extrait aqueux de la plante.

Mots clés : Nanoparticules de ZnO, Aloe Vera, synthèse verte

ملخص :

الهدف الرئيسي لهذا العمل هو اصطناع جسيمات النانو لأكسيد الزنك باستخدام طريقة محافظة للبيئة عن طريق مستخلصات نبات الصبار. العملية المستخدمة غير مكلفة و محافظة للبيئة بالإضافة إلى عدم وجود نفايات. تم حرق مسحوق أكسيد الزنك المسترجع عند درجات حرارة 400 و 500 درجة مئوية لمدة 2 و 4 ساعات على التوالي. تم توصيف جسيمات النانو لأكسيد الزنك باستخدام تقنيات : الانكسار السيني وتحويل فورييه للأشعة تحت الحمراء والمجهر الإلكتروني الماسح وتشتت طاقة الأشعة السينية. أظهرت تحاليل تقنية الانكسار السيني هيكلًا زانسيت لأكسيد الزنك بأحجام نانومترية. حجم البلورات المتوسط يبلغ 44.5 نانومتر. أثبتت الأطياف للأشعة تحت الحمراء وجود مستقلبات ثانوية داخل المستخلص و أظهرت المجموعات الكيميائية المتواجدة في المادة المخلقة. تظهر صور المجهرالإلكتروني الماسح جسيمات النانو لأكسيد الزنك بأشكال مختلفة ، كصفائح النانو لأكسيد الزنك مع حواف محددة وأسلاك نانومترية مع تكتل الجسيمات. كشف تحليل تشتت طاقة الأشعة السينية عن التكوين العنصري لجسيمات أكسيد الزنك على وجود الزنك والأكسجين ، مما يؤكد تكون جسيمات أكسيد الزنك النانومترية بالإضافة إلى معادن أخرى في المستخلص المائي للصبار.

الكلمات الرئيسية : جزيئات أكسيد الزنك النانوية ، الصبار ، التوليف الأخضر

- Symbols & Acronyms -

°	degree
%	percent
°C	Celsius degree
μm	micrometer
λ	X-ray wavelength
β	beta
θ	theta
θ_{hkl}	Bragg-diffraction angle
Å	Ångström
a	lattice parameter
c	lattice parameter
cm	centimeter
cm³	cubic centimeter
d	reticular distance
D	average crystallite size
eV	electronvolt
FWHM	half-width of the diffraction band
G	gram
h	hour
K	kelvin
Kg	kilogram
K	shape factor
km²	cubic kilometer
mm	millimeter
m²	cubic meter
Mol	mole
M	molar concentration
MeV	mega electronvolt
nm	nanometer
T°	temperature

AFM	Atomic Force Microscope
BC	Before Christ
CNT	Carbon Nanotubes
CRTI	Industrial Technology Research Center
CVD	Chemical Vapor Deposition
DNA	Deoxyribonucleic acid
EC	European Commission
EU	European Union
EDX	Energy Dispersive X-ray Spectroscopy
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared spectroscopy
JCPDS	Join Committee on Powder Diffraction Standards
NPs	Nnoparticles(s)
PVD	Physical Vapor Deposition
SEM	Scanning Electron Microscopy
STM	Scanning Tunnelling Microscope
U.S	United States
XRD	X-ray Diffraction

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Genral Introduction

Over the last decade nanotechnology has experienced a real expansion due to its extraordinary potential to manipulate matter at the nanometric scale. This will enable us to explore the fascinating world of nanotechnologies and discover the new characteristics and properties that matter acquires at this scale.. Nanomaterials display advanced features such as photocatalytic activity, antibacterial activity and biocompatibility.

One of the most interesting features of nanoparticles is their high surface-to-volume ratio, which makes them more reactive than bulk materials. Advances in nanoscience are opening up new fields of application in medicine, chemistry, biotechnology, biosensing and more. Various chemical and physical methods have been widely used to produce nanoparticles, including hydrothermal synthesis, sol-gel, laser ablation and lithography. In addition to requiring special equipment and skilled personnel, these methods are toxic and hazardous to health. Chemical synthesis, for example, uses toxic reducing agents such as sodium borohydride (NaBH4), N,N-dimethylformamide (DMF) or hydrazine hydrate, all of which cause damage to the environment.

An ecological approach can solve this problem. Indeed, many efforts are being made to develop an easy, reliable and efficient green synthesis process. Today, the biosynthesis of nanoparticles is still in progress. This method is environmentally friendly and reduces the use of hazardous substances, as the process uses natural materials such as leaves, roots, flowers, extracts and micro-organisms such as bacteria, fungi, algae, etc. Nanoparticles produced by the green synthesis method are cost-effective, non-toxic, stable, more reliable and well-functionalized, particularly in biomedical applications.

- 2 -

Recent studies have focused on the green synthesis of metal oxide nanoparticles, where metal oxides such as zinc, gold, copper, silver, nickel, etc. are gaining importance. One of the most advanced materials is zinc oxide (ZnO), which has some very interesting properties. In its natural state, it is ruby red and abundant in ores, while artificially prepared ZnO is colorless or white. While the properties of natural ZnO have long been known, researchers have recently turned their attention to artificially produced zinc oxide.

The present work will explore a green synthesis method to produce ZnO nanoparticles from extracts of a plant "Aloe barbadensis miller", commonly known as "Aloe Vera". The ambition is to develop low-cost green nanomaterials for biomedical and/or cosmetic applications.

The manuscript will consist of three chapters and a general conclusion. The first chapter will be devoted to a literature review, and will give a brief overview of nanotechnologies and explore nanoparticles in depth (types, fields of application, properties, synthesis processes). It will focus in particular on zinc oxide nanoparticles and give a detailed description of the plant material used for their biosynthesis. The second chapter will describe the elaboration of ZnO NPs by the sol-gel route, and the final one will be devoted to discussion and interpretation of the results obtained. The manuscript will end with a general conclusion.

Chapter 1 : State of Art

I.1. Nanotchnology & Nanoparticles

I.1.1. Introduction to nanotechnology

Today, the field of nanotechnology is rapidly expanding, and is set to be the core of the industrial revolution. Nanotechnology is a combination of two words: "nano", meaning small, and "technology". So it is the technology that deals with small things.

The term nanotechnology refers to the study, processing and manipulation of materials at the atomic, molecular and sub-molecular scales, in other words, at dimensions ranging from 1 to 100 nm. One nanometre is around 500,000 times thinner than the line of a ballpoint pen, about 30,000 times thinner than the thickness of a human hair, and 100 times smaller than a DNA molecule [1].
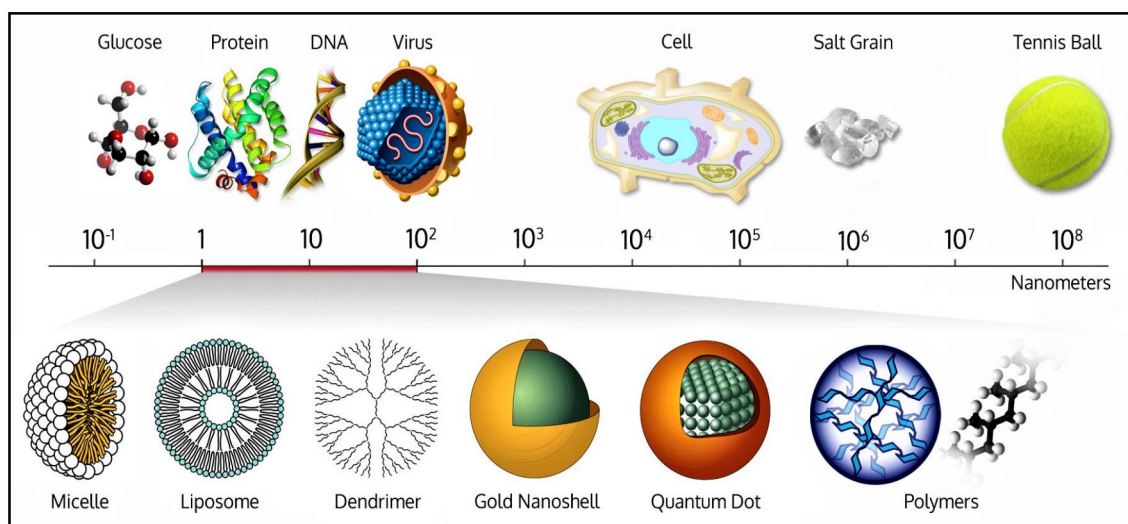
Figure 01 : Scale representing various objects and their orders of magnitude in comparison with the nanometer.

Materials at nanometric scale draw particular attention, thanks to their thermal, electrical, magnetic and optical properties, which differ from the corresponding solid material. The singular properties displayed by these nanomaterials are attracting more and more interest among researchers and scientists of different disciplines, as they offer a promising range of applications in medicine, information technology, electrical and food industries.

I.1.2. History of nanotechnology
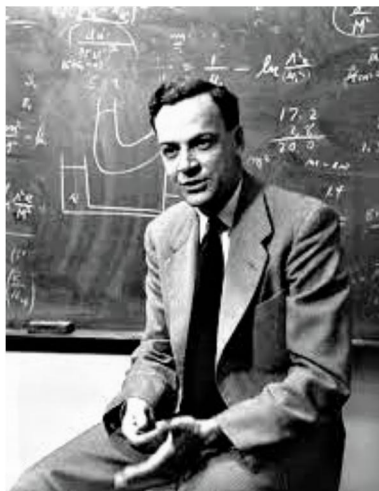
During a presentation in 1959, physicist Richard Feynman declared: "The principles of physics, as far as we can judge, are not opposed to the possibility of manipulating things atom by atom". With these words, the American physicist suggested that the scientific community should explore the universe of the extremely small.

The word "nanotechnology" was first used in 1974 by Norio Tanigushi. In the 1980s, with the discovery of the scanning tunnelling microscope (STM), and later the atomic force microscope (AFM), the nano world really opened up to researchers. Thanks to the extreme precision of their tools, scientists were able to start manipulating atoms one by one.

I.1.3. Nanomaterials & nanoparticles

I.1.3.1. Definition of nanomaterials

Nanomaterials are materials with at least one structural dimension ranging from 1 to 100 nanometers [1]. This small size gives them physical and chemical properties that stand out from those of "conventional" materials.

I.1.3.2. Definition of nanoparticles

Nanoparticles are usually considered to be a group of atoms or molecules linked together with a ray of less than 100nm. Considered as a subdivision of bulk material, we can conveniently define them as an aggregate or set of atoms with at least one or more of their external dimensions ranging from 1 to 100nm.

Depending on how many dimensions are on the nano scale, four categories of nano-objects can be distinguished:

- ❖ **Zero Dimension :** If none of the dimensions are on the nanoscale. We are dealing with **clusters**.
- ❖ **One Dimension:** If only one dimension is nanoscale, we talk about **nanotubes, fibers** and **rods**.
- ❖ **Two Dimension:** If two dimensions are in the nanometer range, we speak of **nanofilms** and **coats**.
- ❖ **Three Dimension:** If all three dimensions are between 1-100 nm. We have **nanomaterials** such as ceramics and nanostructured metals**.**

| Clusters | Nanotubes, fibers and rods | Films and coats | Polycrystals |
| 0D | 1D | 2D | 3D |
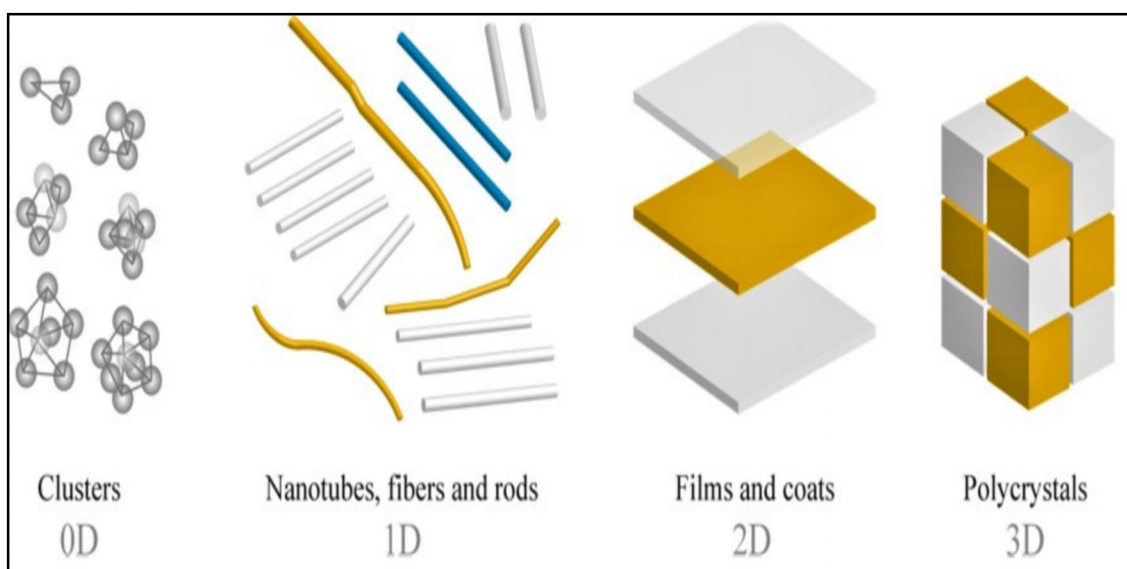
Figure 02 : Classification of Nanomaterials (0D) spheres and clusters, (1D) nanotubes, fibers, and rods, (2D) films and coats, (3D) nanomaterials.

I.1.3.3. Regulation & Recommendation

In August 2022, the European Commission released, for legislative purposes, a recommendation on the definition of nanomaterials. This document aims to update the definition included in Recommendation 2011/696/EU, taking into account scientific progress.

In the current Article 2(k) of the EU Cosmetics Regulation, a nanomaterial is defined as "an intentionally manufactured insoluble or biopersistent material having one or more external dimensions, or an internal structure, in the range from 1 to 100 nm" (EC, 2009) [1].

Meanwhile, the European Commission's Recommendation 2011/696/EU defines a nanomaterial as "a natural, accidental or manufactured material containing particles, in an unbound state or in the form of an aggregate or agglomerate, in which, for 50% or more of the particles within the grain size distribution, one or more external dimensions are in the size range from 1 nm to 100 nm". Where justified by environmental, health, safety or competition concerns, the limit of 50% of the particle size distribution may be replaced by a limit between 1 and 50%" (EC, 2011) [1]. The table below summarizes the main elements of the definition of nanomaterials, comparing the 2011 and 2022 recommendations [1].

Table 01 : Comparative overview of the main elements of the definition of nanomaterials between the 2011 and 2022 European recommendations [1].

2011 EC Recommendation	2022 EC Recommendation
Natural, accidental or manufactured materials, in raw, aggregate or agglomerate form.	Natural, accidental or manufactured material made up of solid particles present either alone or as identifiable constituent particles in aggregates or agglomerates.
When 50% or more of the particles in the number size distribution have one or more external dimensions in the size range 1 nm to 100 nm. In specific cases and when justified by environmental, health, safety or competitive concerns, the 50% threshold of the number size distribution may be replaced by a threshold between 1 and 50%. ❖ As an exception, fullerenes, graphene flakes and single-walled carbon nanotubes with one or more external dimensions smaller than 1 nm are considered nanomaterials.	When 50% or more of these particles in the number-based size distribution meet at least one of the following conditions: ❖ One or more external dimensions of the particle are between 1 nm and 100 nm. ❖ The particle has an elongated shape, such as a rod, fiber or tube, with two external dimensions less than 1 nm and one greater than 100 nm. ❖ The particle has the shape of a plate, one external dimension of which is less than 1 nm and the other dimensions of which are greater than 100 nm.
When it is technically possible and required by specific legislation, conformity with the definition can be determined on the basis of specific surface area per volume :	When defining the particle size distribution is based on the number of particles :

-Materials should be considered to meet the definition when their specific surface area per volume is greater than 60 m²/cm³. -However, a material which, on the basis of its particle size distribution, is a nanomaterial may be considered as conforming to the definition even if its specific surface area is less than 60 m²/cm³.	-Particles with at least two orthogonal external dimensions greater than 100 µm should not be taken into account. -However, a material whose specific surface area per volume is <6m²/cm³ is not regarded as a nanomaterial.

I.1.3.4. Classification of nanoparticles

Nanoparticles can be classified according to numerous criteria, such as composition, dimension and origin.
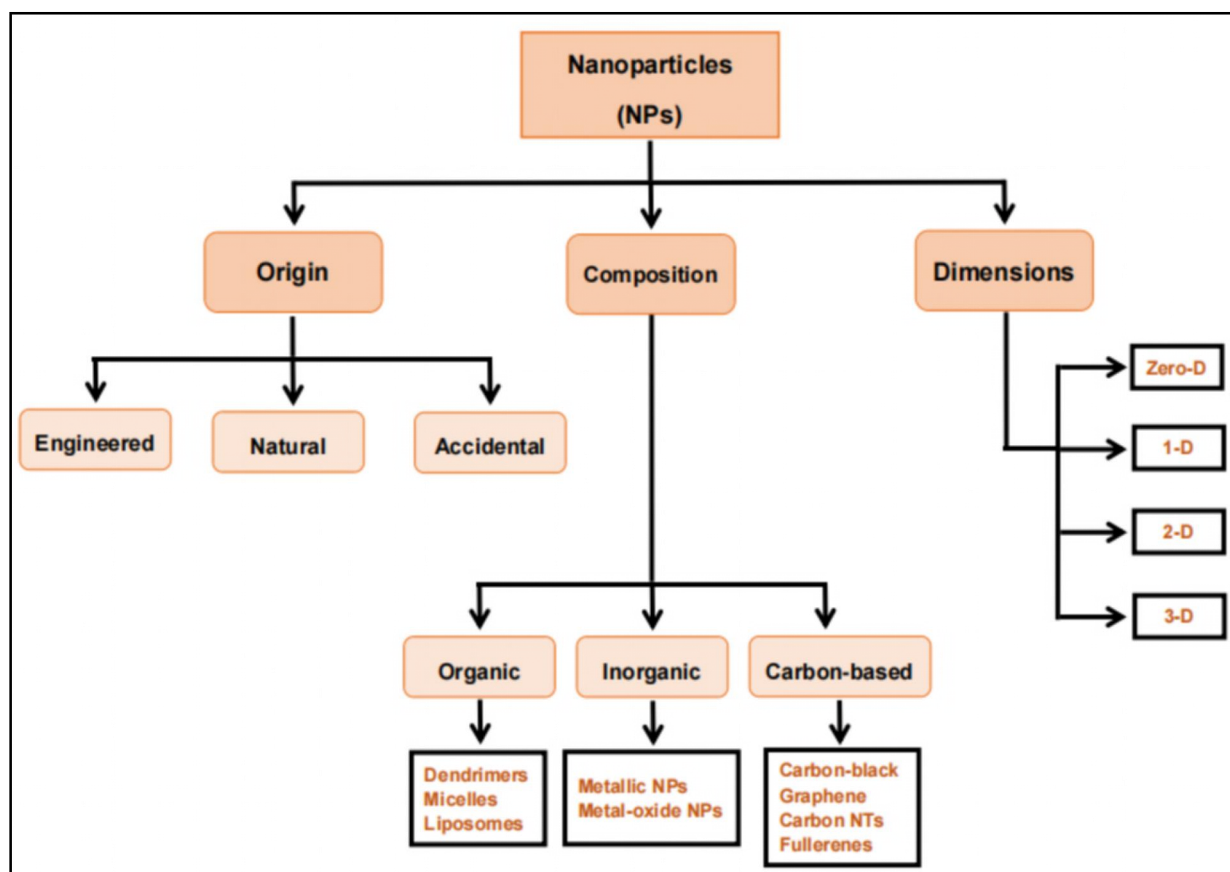
Figure 03 : Classification of nanoparticles according to their origin, composition and dimension.

I.1.3.4.a. Classification of nanoparticles according to their origin of emission

❖ **Nanoparticles from natural sources :** A very large number of nanoparticles are released into the environment, including dust emitted by combustion or volcanoes, wastewater, photosynthesis, forest fires and sandstorms...

❖ **Nanoparticles either not manufactured or manufactured by man :** This category includes atmospheric particles, emitted notably by diesel and gasoline-powered vehicles and urban heating systems. Other nanoparticles are non-intentionally produced by man, such as those present in welding smoke.

❖ **Industrially manufactured nanoparticles :** They are present in tires, shoe soles, white paints, toothpastes, sunscreens and catalysts....

I.1.3.4.b. Classification of nanoparticles according to their composition

❖ **Carbon-based NPs :** These nanoparticles generally contain carbon and are found in morphologies such as hollow tubes, ellipsoids or spheres. Fullerenes (C_{60}), carbon nanotubes (CNT), carbon nanofibers, carbon black, graphene (Gr) and carbon onions are included in the category of carbon-based NPs. Laser ablation, arc discharge and chemical vapor deposition (CVD) are the main methods of manufacture for these carbon-based materials (except for carbon black) [15].

❖ **Inorganic NPs :** These are metal and metal oxide nanoparticles. These NPs can be synthesized as metals such as Au or Ag NPs, metal oxides such as TiO_2 and ZnO NPs, and semiconductors such as silicon and ceramics [15,16].

❖ **Organic NPs :** These are nanoparticles manufactured mainly from organic material, with the exception of carbon-based or inorganic NPs. The use of non-covalent (weak) interactions for self-assembly and molecular design helps transform organic NPs into desired structures such as dendrimers, micelles, liposomes and polymeric NPs [17,18].

❖ **Composite NPs :** Nanocomposites are multiphase nanoparticles and nanomaterials, with a nanoscale phase that can combine NPs with other NPs or NPs with larger or bulk materials (e.g. hybrid nanofibers) or with more complex structures, such as organometallic armatures. Composites can therefore be any combination of carbon-, metal- or organic-based NPs with any form of bulk material like metal, ceramic or polymer [18].

I.1.3.4.c. Classification of nanoparticles according to their function in the material

❖ **Nano-reinforced materials :** Nano-objects are incorporated or manufactured in a matrix to provide new functionality or modify physical properties. Nano-composites are a good example of a reinforcement that provides superior abrasion resistance [2,6].

❖ **Surface nanostructured materials :** Nano-objects are used to create surface coatings. The manufacturing processes for these surface coatings are based on physical (PVD) and chemical (CVD) deposition principles [2,6].

❖ **Volume nanostructured materials :** Nano-objects can also be parts of bulk materials which, thanks to their nanometric structure (porosity, microstructure, nanocrystalline network), exhibit specific physical properties [2,6].

I.1.3.5. Properties of nanoparticles

I.1.3.5.a. Properties of NPs related to their size

As particle size decreases, new properties and behaviors emerge. Isolating, opaque materials may become conductive or transparent, or even change color, they might turn soluble, or spontaneously form ordered structures. This evolution of properties occurs when we reach dimensions of less than 50 nm. The shape of nanoparticles also influences their optical, catalytic and charge transport properties.

Also, as size decreases, the surface-to-volume ratio becomes greater, and surface properties eventually become more important than the mass involved. The most demonstrative example of the influence of surface area is given by [2], picturing a 50kg piece of quartz (SiO2) in cubic form.

The cube is 27cm long, and its surface area is around 0.44m². By reducing the length of the cube's sides to 1mm, the surface area of the new cube reaches 120m², and by reducing to 5 nm the total surface area of the quartz reaches 2km². This is illustrated in the figure below:
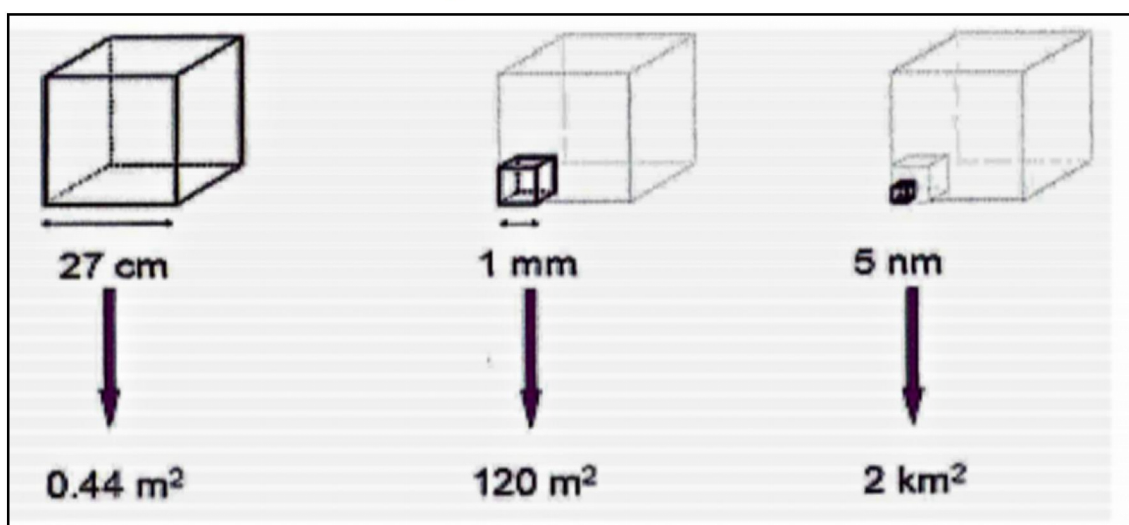
Figure 04 : Diagram showing how surface area is increased by decreasing particle size (cubes).

I.1.3.5.b. Properties of NPs related to their surface area

The surface of nanoparticles is important for their chemical reactivity and ability to adsorb molecules. The presence of charges on these surfaces helps nanoparticles to interact with their environment. NPs display chemical characteristics on their surface that are not identical to those present in their depth. The different surface properties influence the activity of these particles in the biological environment : Inhaled particles exhibit a number of interactions with the biological environment that occur at the particle surface, either with extracellular fluids or with the cells themselves.

I.1.3.6. Applications of nanoparticles

Nanoparticles are applied in almost every area of our daily lives. The strength of nanoparticles lies in their surface-to-volume ratio. As a result, the surface area of the material in question increases by almost 5000 times from the centimetric to the nanometric scale [2]. They have unique properties that make them useful for many applications, such as :

❖ **Medical, pharmaceutical, biomedical and biotech :** drugs and active agents, drugs delivered only to specific organs, biocompatible surfaces for implants, oral vaccines, bone and tissue regeneration, self-diagnostic kits [6,10]. antiallergenic medical adhesive surfaces, medical imaging... [25].

❖ **Cosmetics and perfume industry :** to improve the properties of cosmetic products, such as optical properties, hold, transparency and shine [3]. Transparent sunscreens, make-up with better hold, toothpaste etc [23].

❖ **Automobile, aeronautics and aerospace :** Reinforced and lighter materials, brighter exterior paints, scratch-resistant coatings, sensors to optimize engine performance, ice detectors on aircraft wings, diesel additives for improved combustion, more durable and recyclable tires... [21].

❖ **Chemistry and materials :** Multifunctional catalysts, corrosion inhibitors, pigments, fillers, ceramic powders, antibacterial and ultra-resistant textiles and coatings... [24, 25, 26].

❖ **Food industry :** active packaging, additives, colorants, anti-agglomerants, emulsifiers... [23].

❖ **Construction :** self-cleaning and anti-pollution cements, self-cleaning and anti-fouling glazing, paints, lacquers, adhesives, sealants... [22, 23].

❖ **Energy, Electronics and Communications :** next-generation photovoltaic cells, pocket-sized electronic libraries, ultra-fast computers, wire-free technologies, flat screens... [22]. new types of batteries, smart windows, more efficient isolating materials, hydrogen fuel storage... [21].

❖ **Defense :** Chemical and biological agent detectors and correctors, miniaturized surveillance systems, more precise guidance systems, lightweight self-repairing textiles [6].

❖ **Environment and ecology :** Reduction of carbon dioxide emissions, production of ultrapure water from seawater, more effective and less damaging pesticides and fertilizers, specific chemical analyzers... [21].

Figure 05 : Some application areas for nanomaterials

I.1.3.7. Synthesis of nanoparticles

I.1.3.7.a. Methods for manufacturing nanoparticles

Numerous techniques are available for manufacturing nano-objects, for which several parameters need to be controlled: size and shape in particular. Two main approaches coexist in the field of nanomaterials :

The first, known as "top-down", consists in miniaturizing existing devices by means of size reduction. The opposite approach, called "Bottom-up", involves assembling atomic or molecular patterns to form nanometric objects [19, 20].
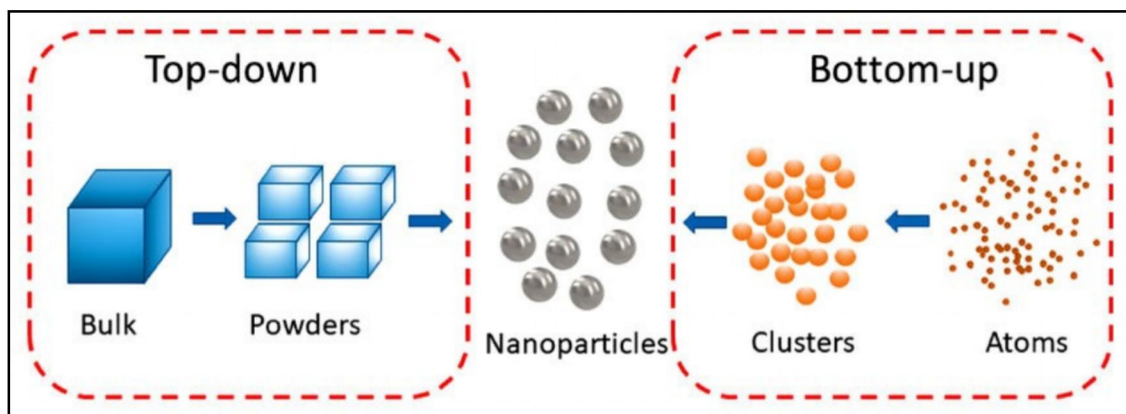
Figure 06 : Scheme of top-down and bottom-up synthesis of nanoparticles.

I.1.3.7.b. Methods for the synthesis of nanoparticles

❖ **Chemical synthesis :** There are several techniques for manufacturing nanoparticles by chemical routes, widely used in the industry. For vapor-phase reactions, vaporized precursor materials are introduced into a CVD (Chemical Vapor Deposition) reactor, where the precursor molecules are adsorbed onto the surface of a substrate maintained at a suitable temperature. Reactions in liquid media lead to synthesis and are usually carried out using an aqueous or organic solution containing the reactants. Nanoparticle precipitation is achieved by modifying the physico-chemical balance conditions, either by chemical co-precipitation or hydrolysis. Finally, sol-gel techniques are used to produce nanomaterials from alkoxide precursors via polymerization reactions.

❖ **Physical and mechanical synthesis :** Nanoparticles can be manufactured using a vapor phase derived from a source material by heating (crucible or crucible-free melting) or bombardment (electron beam, pyrolysis, laser). In most cases, the vapor of the solid to be formed is cooled by collisions with a neutral gas, and the material is collected on a cold wall. Another way of obtaining nanopowders is to use microwaves on millimeter-sized powders. Thin layers of nanometric thickness can also be produced by PVD (Physical

Vapor Deposition). Mechanical synthesis" generally involves grinding micrometric powders (1 to 30 µm). It produces homogeneously dispersed nanoprecipitates or nano-objects. Densification techniques consist in converting a powdered material into a solid part, and involve two stages: a mechanical compaction operation and a sintering operation. Hot isostatic pressing allows these two operations to be carried out in a single step. Highly deformable techniques (torsion, extrusion, etc.) are also being developed to obtain nanocrystals and nanostructures.

❖ **Biological synthesis :** Several biological sources such as plant extracts, bacteria, actinomycetes, fungi, yeasts, viruses, macro-algae, aquaculture and horticultural food waste are already being introduced as precursors to produce stable, well-functionalized nanomaterials, where these precursors act as reducing agents.
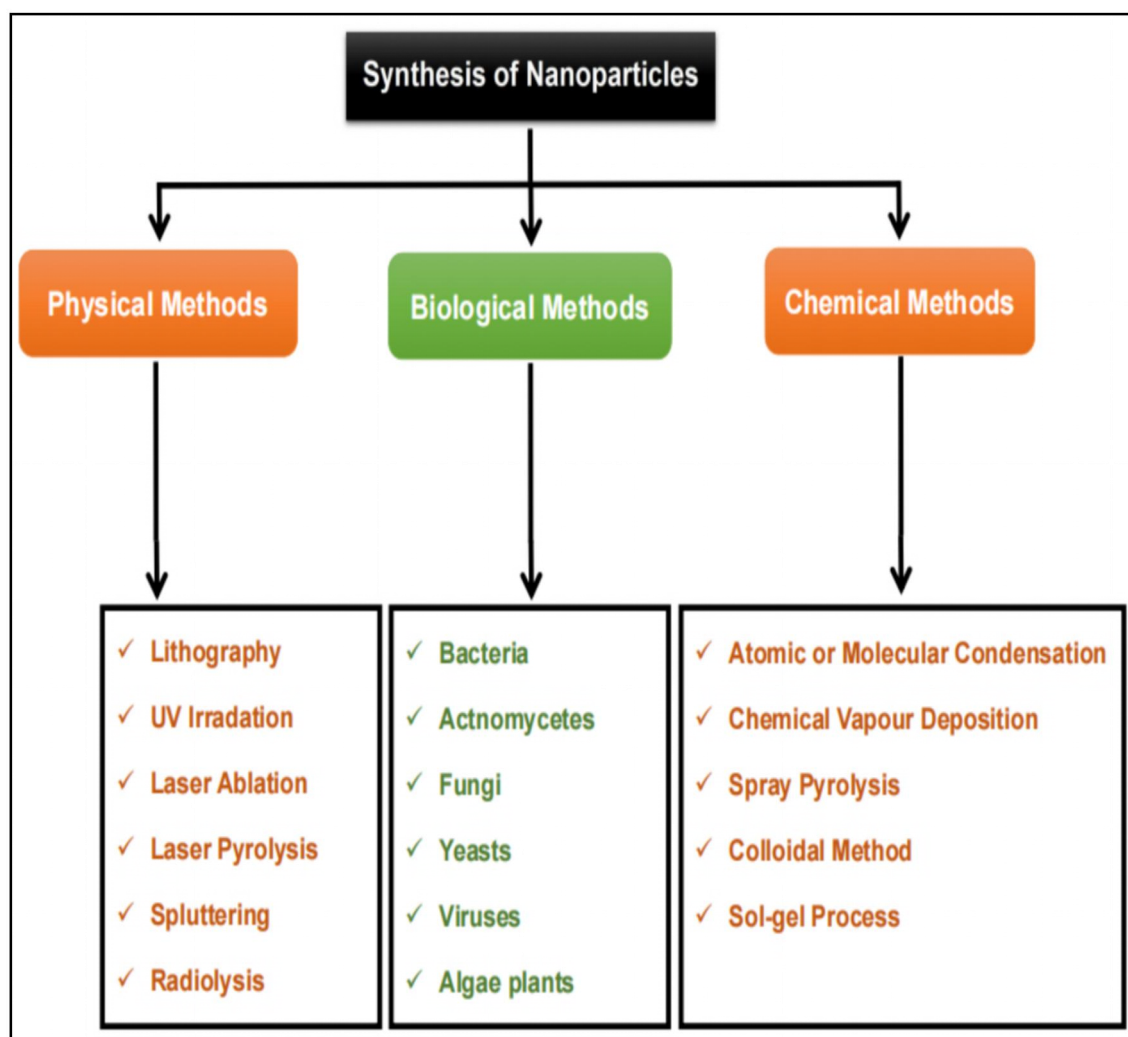
Figure 07 : Different approaches for nanoparticles synthesis. Nanoparticles can be synthesized through physical, chemical, and biological routes.

I.1.4. Zinc oxide nanoparticles

I.1.4.1. Overview on Zinc Oxide Nanoparticles

I.1.4.1.a. Zinc element

The metal zinc (Zn) was discovered in the 13th century BC in India during the extraction of calamine ore. The first industrialization was carried out by William Champion in 1738 [2].

Zinc is an element of the transition metal family, in group II (column 12 of the Mendeleev periodic table), it has the following electronic configuration: $[Ar]\ 4s^2\ 3d^{10}$. The most common oxidation state of zinc is +II [2].

It is a blue-gray metal that can react with moisture, oxygen, and carbon dioxide to form, for example, an insoluble, adherent, and protective layer of zinc carbonate. In contact with water, whitish stains consisting of zinc hydroxide and zinc oxide in particular may appear. These powdery products, also called white rust, are generally not very adherent and not protective. Zinc also reacts with diluted acids, releasing hydrogen [2].

I.1.4.1.b. Zinc oxide

Zinc oxide is found in three crystallographic forms: the cubic form (**Rocksalt**), the **blende** form, and the hexagonal form (**Würtzite**). The most thermodynamically stable is the compact hexagonal structure, called **zincite**, with a Würtzite-like structure, shown in Figure with the following crystal lattice parameters :   **a = 3,25 Å   c = 5,12 Å.**
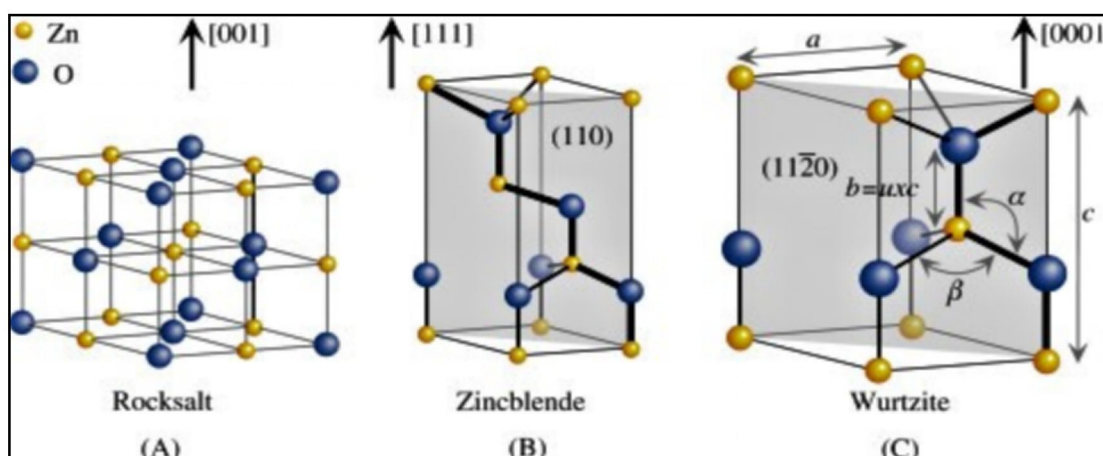
Figure 08 : Schematic representation of the different crystal structures of ZnO.

Each zinc atom is surrounded by four oxygen atoms disposed at the vertices of a tetrahedron. The zinc atom is located at 0.11 Å in a direction parallel to the c-axis of the tetrahedron center. The oxide molecules maintain their individuality, contrary to what one would expect from a purely ionic crystal [2]. Based on the ionic radius values of the cation and anion, the zinc and oxygen atoms occupy only 40% of the volume of the crystal, leaving empty spaces of radius 0.95 Å [2].

Under certain conditions, excess zinc atoms can be accommodated in these spaces at interstitial positions. This feature can explain some of the special properties of ZnO, related to the phenomena of semi-conductivity, photoconductivity, and luminescence, as well as the catalytic and chemical properties of the solid [2].

I.1.4.2. Properties of Zinc Oxide Nanoparticles

ZnO nanoparticles are metal oxide nanoparticles with a band gap of 3.3 eV and a high binding energy (60 MeV), they are categorized as very hard materials. ZnO nanoparticles are nontoxic, nearly insoluble in water, show high selectivity for cancer cells, and are in the appearance of white powder. ZnO NPs have good photocatalytic properties in the ultraviolet range [3]. The table summarizes the general properties of zinc oxide nanoparticles [3].

Table 02 : General properties of zinc oxide nanoparticles

Chemical structure	ZnO
Molecular weight	81.389 g/mol
Appearance	White solid
Odour	Odourless
Crystal structure	Wurtzite
Solubility	Insoluble in water
Density	5.606 g/cm3
Band gap energy	3.37 eV

I.1.4.2.a. Electrical properties

ZnO is a direct-gap semiconductor [11,12]. Bandgap value varies according to preparation method and concentration ratio. It lies between 3.3eV and 3.4eV. The electrical properties of ZnO crystals are highly dependent on the method and thermodynamic conditions under which they are grown [13]. ZnO has a natural n-type electrical conductivity, due to the presence of interstitial zinc atoms. The valence band, formed by electrons ensuring atomic bonds: they remain localized. At T=0°K, the valence band is full. The conduction band, of higher energies, made up of electrons delocalizable to the entire material: they ensure electrical conduction.

✓ For a conductor, the conduction band is partially filled. On the other hand, there is overlap between the valence and conduction bands.

✓ For an isolator, the conduction band is empty, and there is a band gap between the valence band and the conduction band. Its width, called the gap, is of the order of a few eV. Example: about 6 eV for diamond. This gap is too wide for valence electrons to spontaneously jump to the conduction band.

✓ There's a third possibility Semiconductors, characterized by a gap of the order of leV or less. Example: 1.12 eV for silicium, 0.67 eV for germanium. Thermal excitation allows a few valence electrons to pass through to the conduction band: a semiconductor is therefore capable of conducting electricity, but only to a very limited extent. The gap left in the valence band is called a hole.

I.1.4.2.b. Optical properties

ZnO is a transparent material in the visible range, and is of considerable interest for its remarkable properties, such as its bandgap width, which allows it to emit from the visible to the ultraviolet. In addition, its direct gap induces highly efficient radiative recombination.

I.1.4.3. Uses and applications of Zinc Oxide Nanoparticles

Among the several metal oxide nanoparticles, ZnO NPs stand out for their abundance, stability, electrical conductivity, piezoelectricity, non-toxicity, and optical transparency. There are many applications for zinc oxide powder, and the most common are summarized below :

❖ **Medical applications :** Zinc oxide is widely used to treat a variety of skin conditions, in products such as baby powder, diaper rash cream, calamine cream, anti-dandruff shampoos, and antiseptic cream [20]. It is also used by athletes as a patch to prevent damage to soft tissues during training [21].

❖ **Cosmetic applications :** Zinc oxide can be used in ointments, creams and lotions to protect against sunburn and other skin damage caused by ultraviolet rays.

❖ **Electrical applications :** Widely used to protect electronic devices, particularly high-voltage power stations. In solar cells, zinc oxide in nanowire form is incorporated into photovoltaic cells to improve their efficiency. In electrical generators, the piezoelectric properties of nanowires are used to transform mechanical energy into electrical energy. Because of their piezoelectric properties, ZnO films can be used as mechanical detectors, or in electronic devices such as correctors, filters, amplifiers and resonators for radio communications and image processing.

❖ **Rubber manufacturing :** Between 50% and 60% of ZnO nanoparticles production is used in the rubber industry [22]. Zinc oxide with stearic acid is used in rubber vulcanization [23]. ZnO is an additive that also protects the rubber.

❖ **Ceramics industry :** The ceramics industry consumes large quantities of zinc oxide, particularly in the manufacture of glass, porcelain and sintered ceramics, as it reduces the coefficient of expansion and improves stress stability.

❖ **UV absorbers :** Zinc oxide offers good protection against ultraviolet rays, and is used in sun lotions [22], as well as in sunglasses for use in space and as protection for welding.

❖ **Paint industry :** Zinc oxide is also used in the paint industry, as it provides high hiding power, better color retention, greater durability and protection against ultraviolet rays.

❖ **Food additive :** Zinc oxide is added to many food products, including breakfast cereals, as a source of zinc, a nutritional supplement (to boost the immune system). Some pre-packaged foods also contain traces of ZnO.

I.2. Green Chemistry & Biosynthesis

I.2.1. Introduction to Green chemistry

The concept of green chemistry emerged in the United States in the 90s. At the time, the aim was to design chemical products and processes that reduce or even eliminate the use and synthesis of hazardous substances. But it was in 1998 that Paul Anastas and John Warner, researchers at the U.S. Environmental Protection Agency (EPA), laid the theoretical foundations of this new discipline. Green chemistry represents a real break with the chemistry of the 20th and 21st centuries. In the 20th century, the conception and development of chemical processes were essentially focused on optimizing reactions. Today, chemical processes are built on a global concept that takes into account the nature and quantity of the materials involved (raw materials and solvents), the energy required (soft chemistry), the quantity of waste via recycling, and the possibility of analyzing the materials involved at all stages on reduced sample quantities (green analytical chemistry).

Today, the green chemistry industry is faced with five major societal challenges :

-Producing food (agriculture, livestock breeding, etc.)
-Producing medicines
-Producing energy
-Producing potable water
-Protecting the environment

I.2.2. The twelve principles of green chemistry

✓ **Prevent pollution at source :** This means devising a chemical process that avoids the production of future waste residues.

✓ **Saving raw materials :** Saving atoms means being able, within a single raw material, to recover all the molecules that can be used for various

applications in energy, cosmetics and the food industry. This requires powerful separation techniques.

✓ **Work under safer conditions :** This can be achieved by the use of soft operating conditions (ambient temperature, low pressure...) and preferential use of products with little or no toxicity for human health and the environment.

✓ **Designing less toxic chemicals :** We need to develop new molecules that are both more effective and non-toxic. Safety is evaluated by toxicological studies at cellular and at organismal levels.

✓ **Use non-toxic solvents :** This means finding alternatives to toxic and polluting organic solvents such as benzene, chloroform and trichloroethylene, chemical products with a tragic reputation.

✓ **Saving energy :** This means reducing energy costs and developing efficient materials for energy storage. It also means finding new low-carbon energy sources to generate low greenhouse gas emissions.

✓ **Use renewable resources :** Better than using fossil resources; biomass, which represents all the organic matter that makes up plants, trees, animal, agricultural or urban waste, can judiciously be used as a renewable raw material. In the same spirit, this concept can be extended to the use of renewable energies.

✓ **Reduce the use of intermediate molecules :** This means preferring (whenever possible) to use direct reactions. Intermediate stages consume chemical products which inevitably become waste.

✓ **Prefer catalytic processes to conventional ones :** A catalyst is a substance added to a chemical solution to make a chemical reaction possible. It accelerates the rate of reaction by lowering the energy required for two molecules to react with each other. The catalyst leaves the chemical process unchanged, so it can be recycled.

✓ **Design a chemical product with a view to its final degradation :** A chemical product will inevitably end up as waste. Whenever possible, it is best to design with the idea that all or part of the waste it will become can be recycled. It should also be designed in such a way that its future degradation, whether natural or accelerated, does not lead to the creation of hazardous by-products.

✓ **Real-time analysis of chemicals and their footprint in the environment :** This means preventing pollution by directly monitoring chemical reactions. We need to be able to detect and quantify the presence of chemical and biological agents known to be toxic, even in trace amounts.

✓ **Develop fundamentally safer chemistry :** This means choosing chemical raw materials wisely to prevent accidents, explosions, fires and emissions of hazardous compounds. The form of the chemical is also important: a gaseous molecule diffuses more into the environment than the same molecule in solid form.

I.2.2. Literature on the plant material

I.2.2.1. Background

Aloe vera is a subtropical plant with a rich past dating back to biblical times. It has been mentioned down the ages and is one of the most widely used medicinal plants. At the heart of the leaves is a gel-like substance. Early users of aloe discovered that wounds healed faster when the gel was applied - a remarkable exploit in an age long before antibiotic ointments, when infections of minor wounds were often mortal.

Twelve different recipes for the internal and external use of aloe vera are recorded in the Eber papyrus, an Egyptian relic dating from around 1,500 BC. By 400 BC, the properties of aloe vera were widely recognized from China to India. Today, it is cultivated all over the world [9].

I.2.2.2. Description

Aloe is a perennial, succulent, tree-like plant with leaves growing from the base in a rosette shape. Mature plants can reach a height of 2 and a half inches to 4 feet, with an average length of 28 to 36 inches. The leaves have a green coloration ranging from bright green to gray. They are triangular, fleshy, with a serrated edge, and consist of a thick epidermis covered with cuticles surrounding the mesophyll [9].

Each plant usually has 12 to 16 leaves which, when mature, can weigh up to 3 pounds. Plants can be harvested every 6 to 8 weeks by removing 3 to 4 leaves per plant [9]. Depending on the variety, the plant has single or multiple bicolored flowers and tubular inflorescences that grow in the center of the rosette of the leaves.

The leaves have a high water-holding capacity, which allows the plant to survive in harsh environmental conditions, such as prolonged aridity, and hot and dry climates [10, 15].

I.2.2.3. Biotope & Biodiversity

Table 03 : Cronquist's classification (1981)

Kingdom	Plantae
Subdomain	Tracheobionta
Division	Magnoliophyta
Class	Liliopsida
Subclass	Liliidae
Order	Liliales
Family	Aloeaceae
Genus	Aloe
Species	Aloe vera

With a rich variety of more than 200 species, the aloe finds its genesis in South and East Africa. A large part of them is cultivated in the Mediterranean region, as an outdoor ornamental plant. Thus, Aloe vera has been naturalized in Italy and on the French Riviera [16].

There are numerous sorts of aloe cultivated in the world. However, only two species are commercially cultivated today: Cape Aloe and Barbados Aloe [9,17].

Table 04 : The various species of Aloe Verra [9,17].

Species	Description
Cape Aloes Registered in the French Pharmacopy. 10th Edition	• This variety derives from Aloe ferox Mill and other species growing in those areas (A.africana and perfoliata). • It is native mostly to South and Eastern Africa. It is found in the form of dark brown masses of greenish reflection, with brilliant conchoidal fissures; it has fine transparent blades of a reddish color, and the powder is of a greenish brown. It contains about 18% of hydroxyanthracenic derivatives, calculated as anhydrous aloin. • It is soluble in hot alcohol, partially soluble in boiling water, and almost insoluble in ether and chloroform.
Aloe of Barbados Registered in the French Pharmacopy. 10th Edition	• Derived from Aloe vera L (= Aloe vulgaris Lam). It is also known as the Antilles or Curaçao Aloe. • It comes in hard, opaque masses, with a color ranging from reddish brown to chocolate brown almost black, with a dull or waxy break. The powder is reddish yellow that turns to red-brown in the light.
Aloe Succotrin or Soccotrin	• This species was generated by A. succotrina LAMK and A. perryi BAK, in Arabia at Socotola and in Africa on the coast, where the Arab merchants brought it to Mumbai by the path of Zanzibar. • The drugs were stored in drums and boxes made of gazelle skins and then exported to Europe. • The real aloe succotrin is translucent, nevertheless, there are some which are opaque, and they are the aloes of the leaf which are nowadays very few.

Aloes Caballin (from caballus, horse)	• This aloe is the result of the depository of other commercial species. Some authors report that it is prepared on the coasts of Spain with the different aloes that grow in there and especially with Aloe linguæformis L. • It is found in the form of blackish masses characterized by an empyreumatic smell. In the summer, at high temperatures, it becomes like black pitch.
Aloes from the Natal	• This species is originally from A. candelabrum. It differs from the previous one by its opacity and its grayish-brown color. • It has a different chemical composition, offers a hepatic coloration and its powder has a clear yellow color.

I.2.2.4. Plant anatomy

The first commercial use of aloe was in the 20th century. It consists of a latex substance called aloin, listed in commercial, technical, and governmental literature under the name of "Aloe" [9]. This substance comes from the concentrated suc of the aloe leaves from which a yellow sap spontaneously drips. Aloe juice is irritating and has a very bitter taste. It has been used for many years as a cholagogue, laxative or purgative, depending on the dose (plant in modern therapeutics) [9].
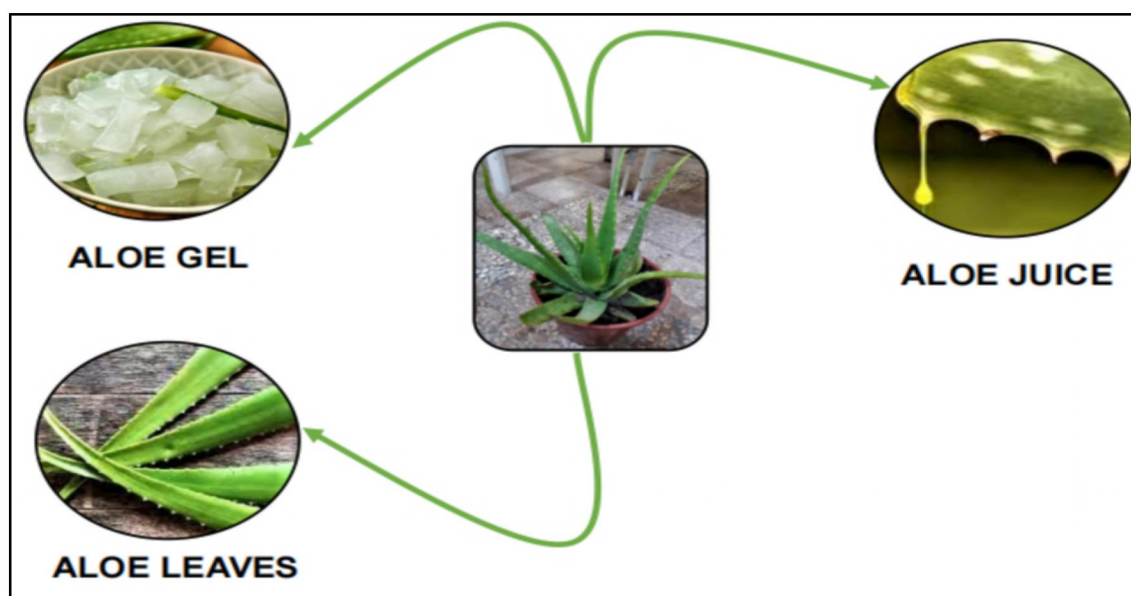
Figure 09 : The main parts of the aloe plant

A little later, another main component of aloe was stabilized and commercialized. It is a clear and colorless semi-solid gel. Aloe book This Gel of Aloe is obtained after the elimination of the most external tissues of the leaf, it is mainly composed by the mucilage of the polyhedral cells of the central zone of the plant [18].

Tradition attributes healing properties to aloe gel, which are due to the stimulation of additives linked to polysaccharides. The great abundance of water gives the gel moisturizing, isolating, and protective properties. Therefore, the gel is widely used in cosmetology as a moisturizing component of liquid or pasty preparations, sun and shaving products, lip balms, ointments, masks, and creams.

I.2.2.5. Chemical composition

I.2.2.5.a. Juice composition

The juice contains **15** to **40%** of **hydroxyantracenic** derivatives which are **C-glucosides** in **10** of the **anthrone aloe-emodol**: **aloin** (=**barbaloin**) and **hydroxy-aloin**. It also comprises a resinous fraction from which were isolated **C-glucosides** of **2-acetonyl-7-hydroxy-5-methyl-chromones** (**aloesone**, **aloeresins A**, **B** (=**aloesine**), and **C**) as well as a **pyronic** derivative, **aloenine** [18].
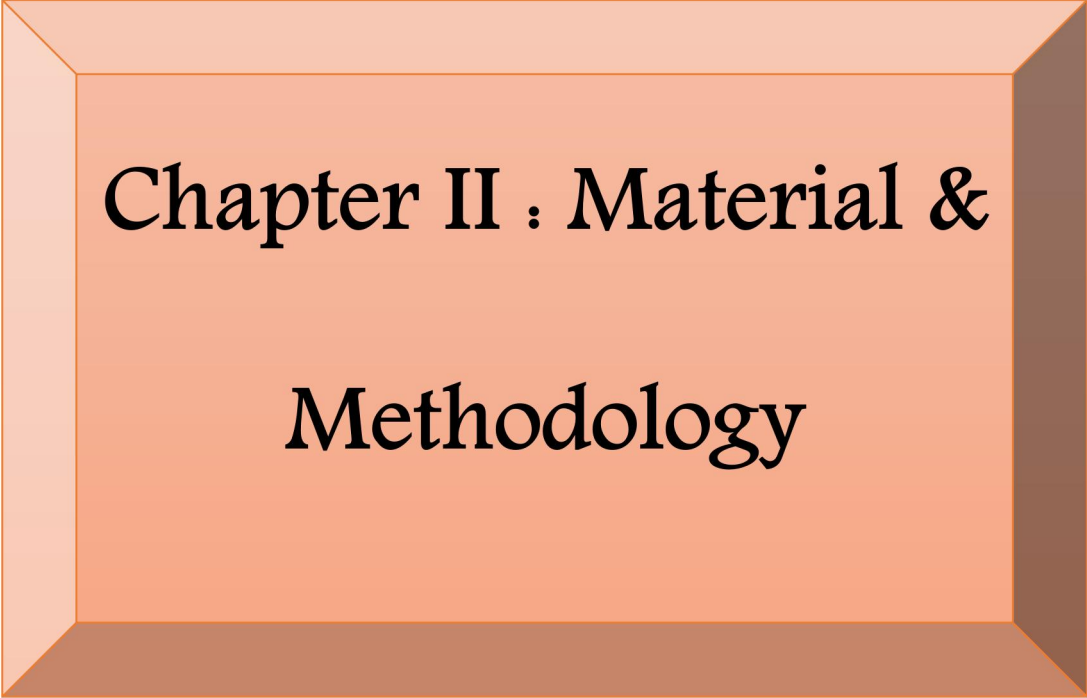
I.2.2.5.b. Gel composition

Chemical analysis has shown that the transparent gel is very rich in water. It also contains amino acids, minerals, vitamins, sterols, enzymes, proteins, and lipids, but mostly polysaccharides (pectins, hemicellulose) and biological stimulators. Later on, the active substances present in the gel were recognised (Acemannans, Carboxypeptidase, Bradykinase, lactate de magnésium, Alprogen, acide salicylique et C-Glycosylchromone) [21].

Table 05 : Biochemical composition of aloe vera [21,22

	Compounds	
Anthraquinones **Anthracene (anthrone)**	- Aloe-emodin - Aloetic acid - Aloin A and B - Anthranol - Barbaloin - Isobarbaloin - Emodin - Ester of cinnamic acid	- Aloe emodin-diglucoside 10-hydroxyaloin A - D-2'-p-Methoxycoumaroylaloeresin B 4,5-dimethyl ether of aloe 6'-malonylnataloin - C-glycosylated anthrone - Aloe emodin-8-O-glucoside
Saccharides	- Cellulose - Glucose - Mannose - Aldopentose - Acetylated mannan (acemannan)	- Glucomannan - Acetylated glucomannan - Galactogalacturan - Glucogalactomannan - Galactoglucoarabinomannan
Phenolic compound	- Sinapic acid - Quercitrin - Kaempferol - Apigenin - Gallic acid - Protocatechuic - Catechin - Vanillic acid - Epicatechin	- Syringic acid - Chlorogenic acide - Gentisic acid - Caffeic acid - Coumaric acid - Ferulic acid - Rutin - Miricetin - Quercetin
Vitamins	- B1 - B2 - B6 - C	- β-carotene - Choline - Folic acid - α-tocopherol

Enzymes	• Amylase • Carboxypeptidase • Catalase	• Cyclooxydase • Lipase • Oxidase
Cinnamic acid	• Chlorogenic acid • Caffeic acid	• Feruloylquinic acid • 3,4-di-O-caffeoyliquinic acid
Flavonoid (O-glycosylated flavonoid)	• Isoquercitrin • Kaempferol-3-O-hexosyl-O-pentoside • Luteolin-8-C-glucoside (orientin)	• Isovitexin • chrysoeriol-7-O-glucuronide • Naringenin-4'-methoxy-O-glucuronide • 5,3'-dihydroxy-6,7,4'-trimethoxy-6,7,4'-trimethoxyflavone (eupatronin)
Chromone	• Aloesin or aloeresin B (C-glycosylated chromone) • Caffeoyl ester of aloesin	• Isoaloeresin • 7-methylether of 2'-feruloylaloesin
Low molecular weight substances	• Arachidonic acid • Cholesterol • Gibberellin • Lectin-like substance • Lignins	• Salicylic acid • β-sitosterol • Steroids • Triglycerides • Uric acid

Chapter II : Material &

Methodology

II.1. Introduction

This chapter is divided into two main parts: the first one concern the preparation of the different extracts of our plant (Aloe Vera), and the second one is dedicated to the biosynthesis of zinc oxide (ZnO) nanoparticles.

II.2. Raw material

II.2.1. Plant material

For this project, we used an officinal species, Aloe Barbadensis Millier.

The plant is about 24 months old and comes from a vineyard in the region of Somaa in Blida, Algiers. It is grown at an altitude of 229 meters, in a Mediterranean climate with an average temperature of 17.9 °C and an average annual rainfall of about 800 mm.

II.2.2. Chemical precursor

The precursor of ZnO NPs used in this project was the zinc sulfate salt. It was supplied by SARL-Biofhetto and came from Sigma Aldrich.

Table 06 : Physical and chemical properties of zinc sulfate

Name	Zinc sulfate
CAS	7733-02-0
Formula	Zn SO4
Structure	
Appearance	Anhydrous zinc sulfate is a colorless crystalline solid
Molecular weight	161.4
Density	3.8 g/cm³
Melting point	680 °C
Function	Precursor

II.3. Synthesis of zinc oxide nanoparticles

II.3.1. The "sol-gel" method

The sol-gel technique is a materials development process enabling the synthesis of glasses, ceramics and organo-mineral hybrid compounds from precursors in solution. It enables thin layers of stacked metal oxide nanoparticles to be produced under "soft chemistry" conditions. The process is carried out at much lower temperatures than conventional synthesis routes. The process can be used in a variety of fields, such as encapsulation and the development of hyper-porous materials, but its main applications lie in the production of thin-film deposits.

The principle of the sol-gel process is based on the use of a succession of hydrolysis-condensation reactions at near-ambient temperature to prepare oxide networks, which can then be heat-treated.

Sol-gel is a combination of a suspension held in a gel-like solid which can be either a colloid or a polymer. The sol-gel process corresponds to the passage from a liquid system called "sol" to a colloidal state called "gel" [7, 8].
The synthesis method of oxide nanoparticles by Sol-Gel starts with the preparation of a homogeneous solution of metallic precursors, and then with a thermal treatment the metallic oxide is obtained in crystalline form [7, 8].

The passage from "sol" to "gel" is carried out firstly by a series of hydrolysis reactions and inorganic polymerization to form a colloidal suspension, then by a process of ageing, and the solid state is obtained by calcination of the "gel". The conditions and the nature of the substances used determine the desired results [7, 8].

Advantages of the sol-gel process : There are many advantages to using the sol-gel process. These include [27] :

✓ Low synthesis temperature compared with conventional ceramization techniques, due to the presence of oxygen in the matrix.
✓ High purity and homogeneity of the final product, thanks to the use of molecular precursors in solution.
✓ Control of nucleation-growth processes during the hydrolysis and condensation phases, notably through the use of chemical modifiers, leading to materials with controlled morphology.

Experimental conditions : The preparation of nanoscale powders requires control of experimental conditions until the optimum parameters are obtained. Important parameters are :

✓ **Solubilization temperature.**
✓ **Calcination temperature.**
✓ **Calcination time**

II.3.2. The general process of zinc oxide formation

The general process of zinc oxide formation is based on three distinct steps. Controlling these steps means controlling the size, shape, and organization of the particles.

❖ **Nucleation:** Elementary particles, called "nuclei" are formed by a process either homogeneous or heterogeneous. The homogeneous nucleation corresponds to the spontaneous condensation of the atoms of the metal; it is a property of intrinsic stability. The nucleation is initiated by the presence of impurities, flaws, or even salts of noble metals such as [AgNO3, K2PtCl4] which constitute the starting point of the growth of particles.

❖ **Growth:** The nuclei thus formed grow, by a phenomenon of crystal growth, until they reach an optimal size. The growth can be described by two mechanisms: (a) the adsorption of atoms on the growing nucleus or (b) the coalescence of clusters. These two types of growth have been observed by F. Fievet's group, during the synthesis in a polyol medium of spherical ZnO nanoparticles of 10 to 20 nm.

❖ **Ostwald maturation:** The nucleation and growth steps are followed by a final step called Ostwald maturation, which results in particles whose size dispersion decreases with time. This maturation of the particles is a thermodynamic phenomenon, which is based on the fact that an interface is expensive in energy.

II.4. Biosynthesis of zinc oxide nanoparticles

II.4.1. Preparation of plant extracts

First, we section a few stems at the basis of the plant. Next, the stems are thoroughly washed with ordinary water and then with distilled water to remove all the dirt, once the stems are dry, they are balanced. Finally, we separate the aloe gel from the leaves.
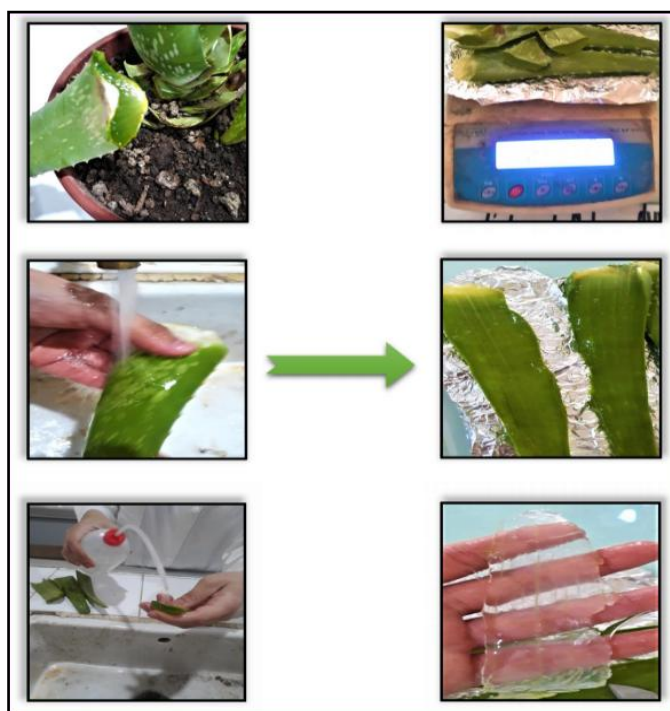
Figure 10 : Separation of the aloe gel from the aloe leaves

II.4.1.1. Leaf extract

The aloe leaves are finely cut and put in a clean beaker previously weighed. The weight of the plant material is recorded.

After the addition of distilled water, the beaker is placed on a stirring hot plate. The temperature is maintained at 80°C for 30 to 45 minutes. The heat will break the membranes of the plant cells and so release the different phytochemicals contained in the aloe leaves.

We proceed to a double filtration first by using a strainer, then with a filter paper, to separate the leaves from their extract. The extract of Aloe is covered with aluminum foil to avoid oxidation of the later in the light, and then preserved in the refrigerator for later use. The waste of leaves is recuperated to put in compost.
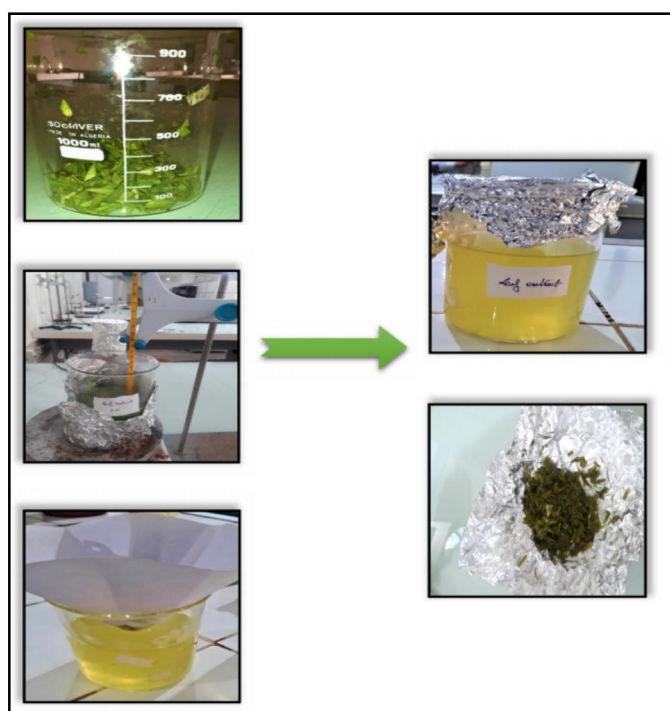
Figure 11 : Preparation of the leaf extract

II.4.1.2. Gel extract

Once the gel is separated from the aloe leaves, it is crushed in a mortar with a pestle and then transferred to a beaker and weighed.

Distilled water is added to the gel then the magnetic bar is introduced. The beaker is covered with aluminum foil to avoid oxidation and put under strong agitation at room temperature for more than an hour.

We proceed to a double filtration with a sieve and then with filter paper. The extract obtained is a homogeneous viscous liquid; the rest of the gel is collected and transferred to a beaker. The two beakers are covered with aluminum foil and stored in the refrigerator for later use.

Figure 11 : Preparation of the gel extract

II.4.2. Preparation of zinc oxide nanopawder

➢ **First experiment :**

1) Preparation of two solutions of ZnSO4 (0.2M). The zinc sulfate salt is measured in two separate beakers, then distilled water is added to each beaker.
2) Each beaker is placed separately on a stirring hot plate, then magnetic bars is been introduced. Stirring is carried out until the zinc salt is completely dissolved.

3) At the same time two burettes are placed on top of the beakers, one is supplied with the leaf extract and the other with the gel extract. While heating and stirring moderately, the extracts are allowed to flow drop by drop, the temperature is kept between 60-80°C.

4) After a while, a change of color is observed for both beakers (reduction of ZnSO4 to ZnO).

Leaf extract + ZnSO4 (0.2M)

Gel extract + ZnSO4 (0.2M)
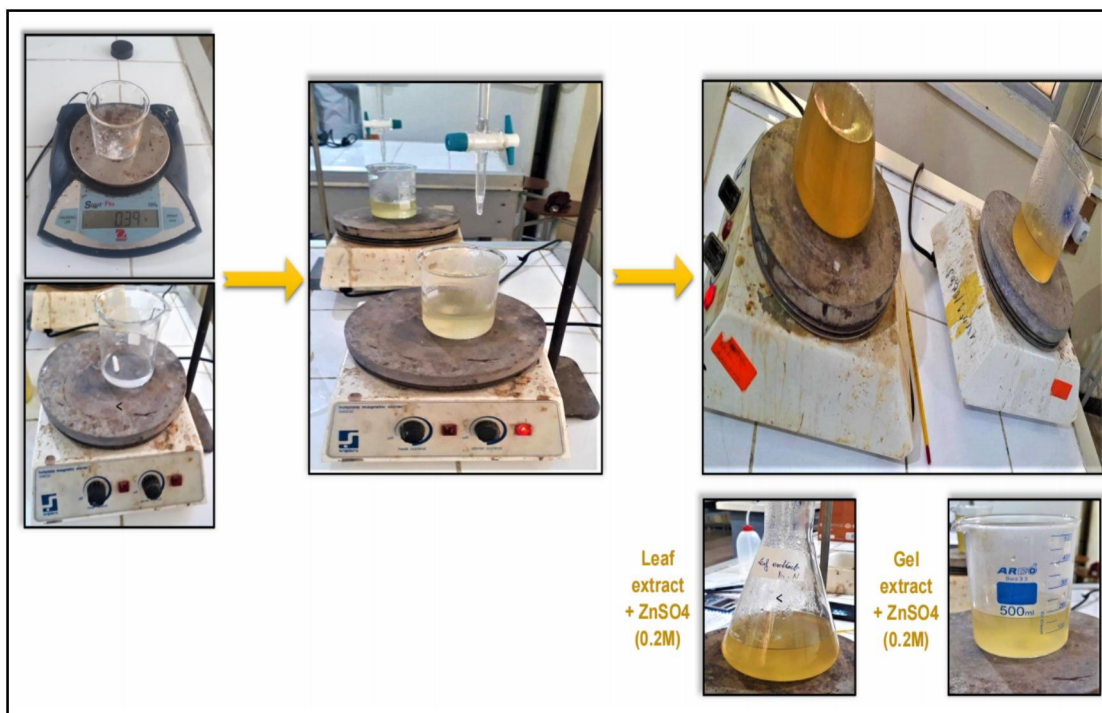
Figure 12 : Biosynthesis if ZnO NPs by sol-gel route.

5) The beaker containing the zinc oxide NPs synthesized from the leaf extract is transferred to a separating funnel. Over time, the ZnO particles settle to the bottom of the funnel, the extra liquid is discarded and the volume of the extract is reduced.

6) Then the beaker is put in the drying oven at 80°C to evaporate the rest of the extract.

7) The solid is transferred into a ceramic container which is weighed beforehand.

8) The zinc oxide nanoparticles are collected after calcination at 500°C, in a sterile plastic bottle. The NPs are stored for later characterization.
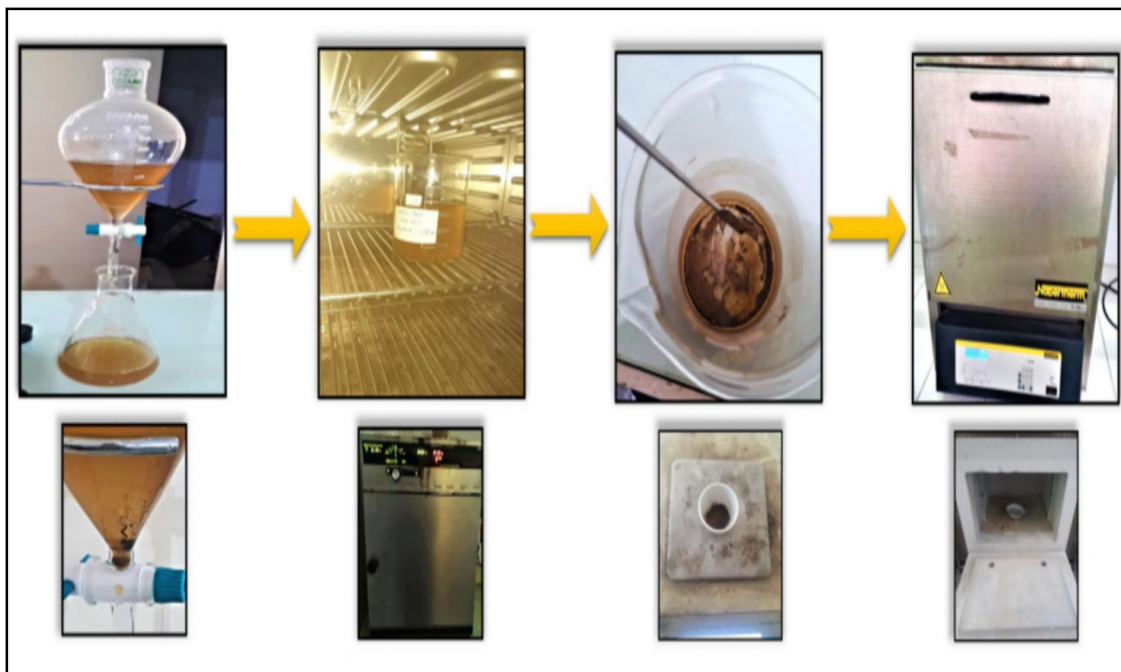
Figure 13 : Recovery and calcination of ZnO NPs synthesised by leaf extract.

9) The nanoparticles synthesized via the gel extract are collected after the passage to the drying oven in a centrifugation tube and then centrifuged twice at a rate of 4500 turns per 15 minutes. Then the NPs are transferred to a ceramic pot for further calcination.
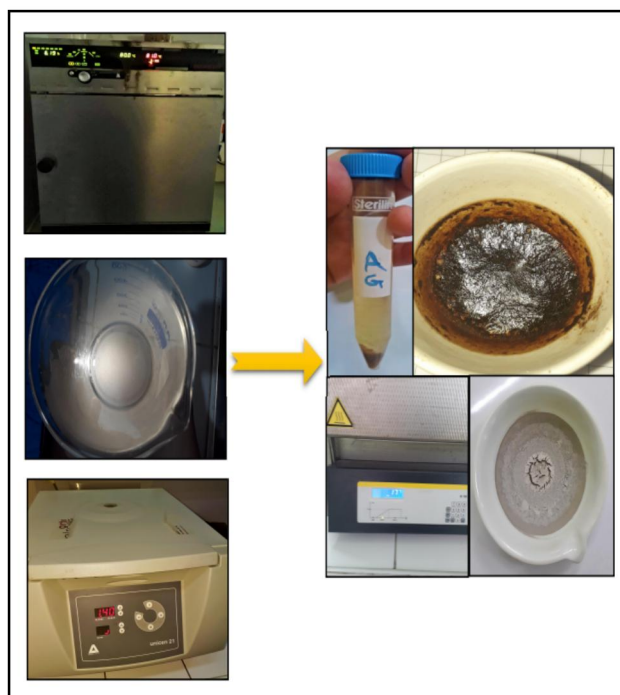
Figure 14 : Recovery, centrifugation and calcination of ZnO NPs synthesised by gel extract.

➢ **Second experiment :**

The second experiment focused on the leaf extract only. Four trials were set up.

Table 07 : Results summary of the second experiment.

Samples	The concentration of the precursor M	Heat °C	Agitation (Color change)
1st sample	0.3	60-80	2.30 h
2nd sample	0.2	60-80	2.30 h
3rd sample	0.3	_	24 h
4th sample	0.2	_	24 h

➢ **Third experiment :**

The third experiment dealt with the gel extract only.

Table 08 : Results summary of the third experiment.

Samples	The concentration of the precursor M	Heat °C	Agitation (Color change)
1st sample	0.3	60-80	4 h
2nd sample	0.2	60-80	4 h
3rd sample	0.3	_	24 h No color change
4th sample	0.2	_	24 h No color change

II.4.3. Proposed mechanism :

The green synthesis mechanism for the synthesis of ZnO nanoparticles is described in Fig 15. The phytochemicals present in the plant extract can act as reducing agents to convert the metal precursors into metal nanoparticles. Phytochemicals are antioxidants and non-toxic compounds; therefore, they can act as both reducing agents and stabilizers. Essential phytochemicals such as flavonoids, phenolic compounds, anthracene, and vitamins have contributed to the reduction process.

The factors including pH, temperature, contact time, metal salt concentration, and phytochemical profile of the plant extract have a significant effect on the synthesis of nanoparticles, the stabilization of nanoparticles, and the number of nanoparticles produced. Makarov et al. proposed that metal ions would be encapsulated as an organic shell in three steps for their stabilization after reduction by plant extracts.

1. Activation phase: involves the reduction of metal ions and nucleation of the reduced metal ions,

2. Growth phase: involved in the stability of the nanoparticles

3. The termination phase: consists of the shape of the formed nanoparticles.

Through the action of phytochemicals, metal ions reach the growth and stabilization phase. The formation of oxygen finally leads to the binding of metal ions, and a definite form is formed. The processes involved in the plant extraction mechanism of nanoparticle synthesis are the preparation of the plant extract, the mixing of the metal solution into the plant extract, and the formation of biocompatible nanoparticles [20].
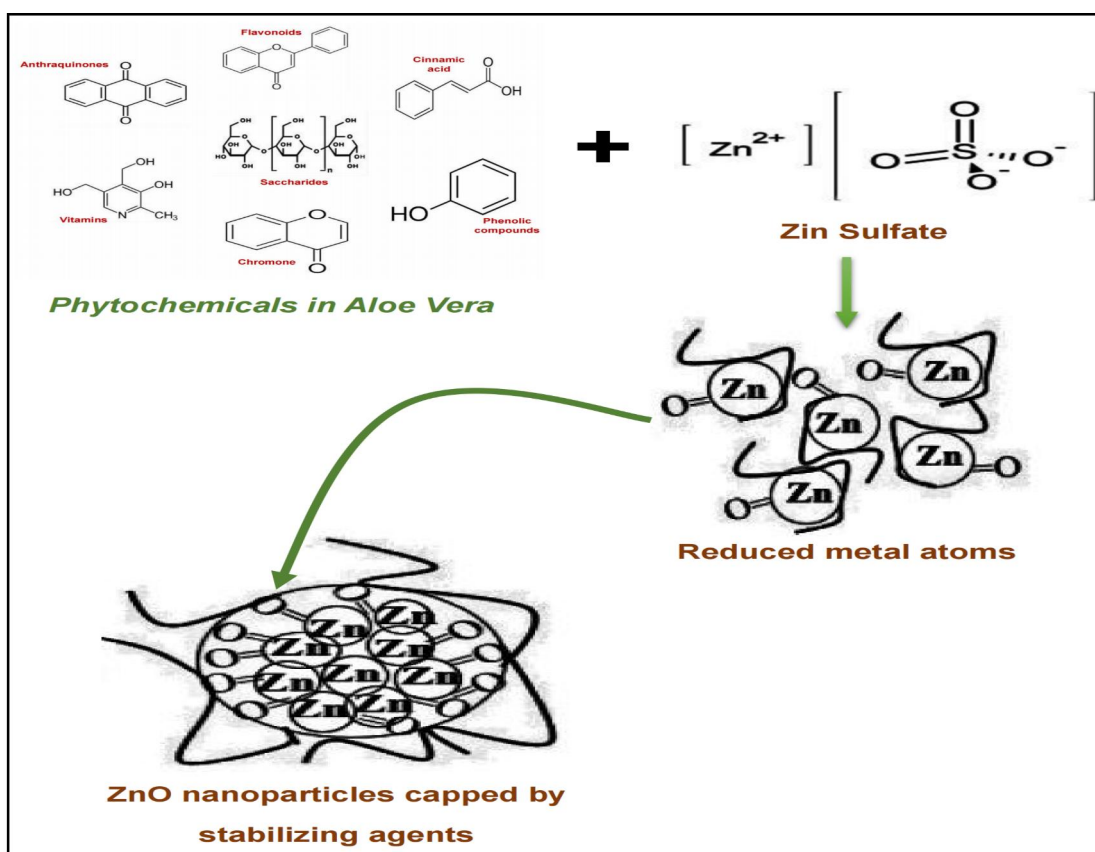
Figure 15 : Mechanism of the biosynthesis of ZnO NPs.

II.5. Methods used for the characterization of zinc oxide nanoparticles

II.5.1. X-ray diffraction (XRD)

X-ray Diffraction (XRD) is a non-destructive rapid analytical technique that is primarily used to determine the structure of a material. It can be applied to crystalline systems, making it easy to identify crystallized phases. It can also be used to determine a number of structural parameters, such as lattice parameters, crystallographic positions of atoms, and the size and orientation of the crystallites making up the material. This technology can be used to measure both the physical and chemical properties of crystalline powders, thin films, epitaxial films, and bulk solid materials.

The X-ray diffraction experimental set-up includes : A monochromatic X-ray tube, sample holder and X-ray photon detector. A goniometric circle on which the X-ray detector moves, and a focusing circle on which the scattered radiation is concentrated before detection.
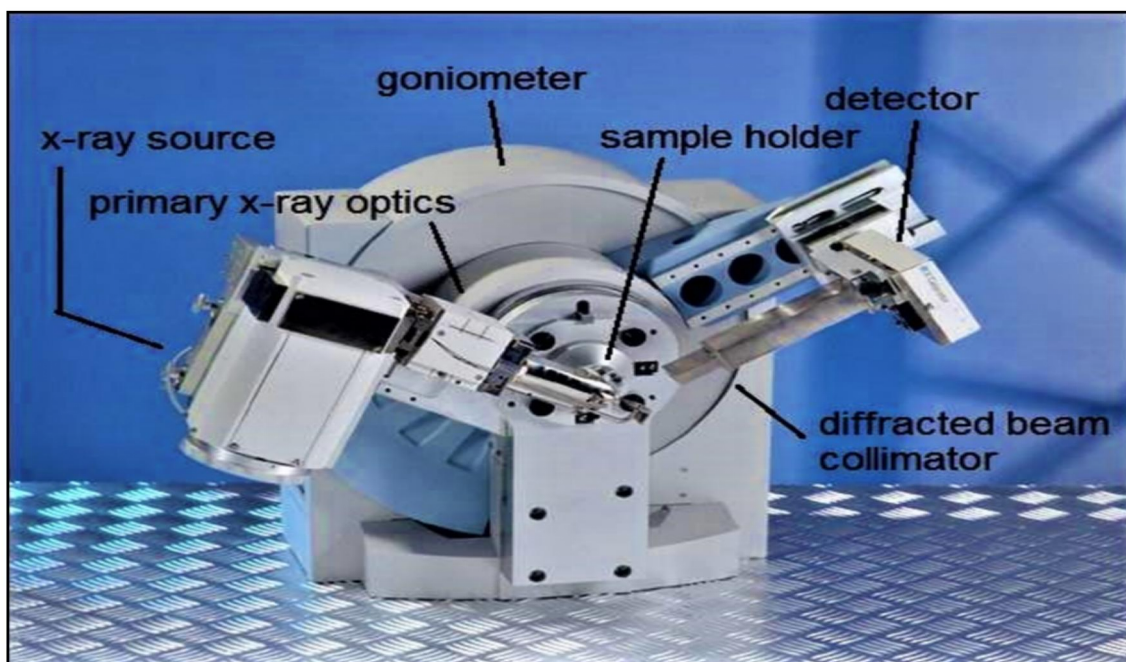
Figure 16 : X-ray diffractometer.

Principle of X-ray diffraction : Incident X-rays are diffracted by the sample and collected by the X-ray photon detector. This detector counts the number of photons received as a function of the angle 2 formed between the detector and the incident X-ray beam. The result is a diffraction pattern showing the intensity of the diffracted photons (number of counts) as a function of 2. The wavelength of the X-rays depends on the type of anticathode used to generate them. Diffraction occurs only in crystallized materials and when **Bragg's** relation is verified: $n \lambda = 2 \, d_{hkl} \sin\theta$

II.5.2. Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra constitute molecular identity cards, and is extremely rich in information. The wavelengths at which the sample absorbs are characteristic of the chemical groups present in the sampled material. Tables can be used to assign absorption bands to the various bonds present in the compounds. By consulting the tables and cross-referencing the results, it is possible to assign the bands and identify the corresponding chemical groups.
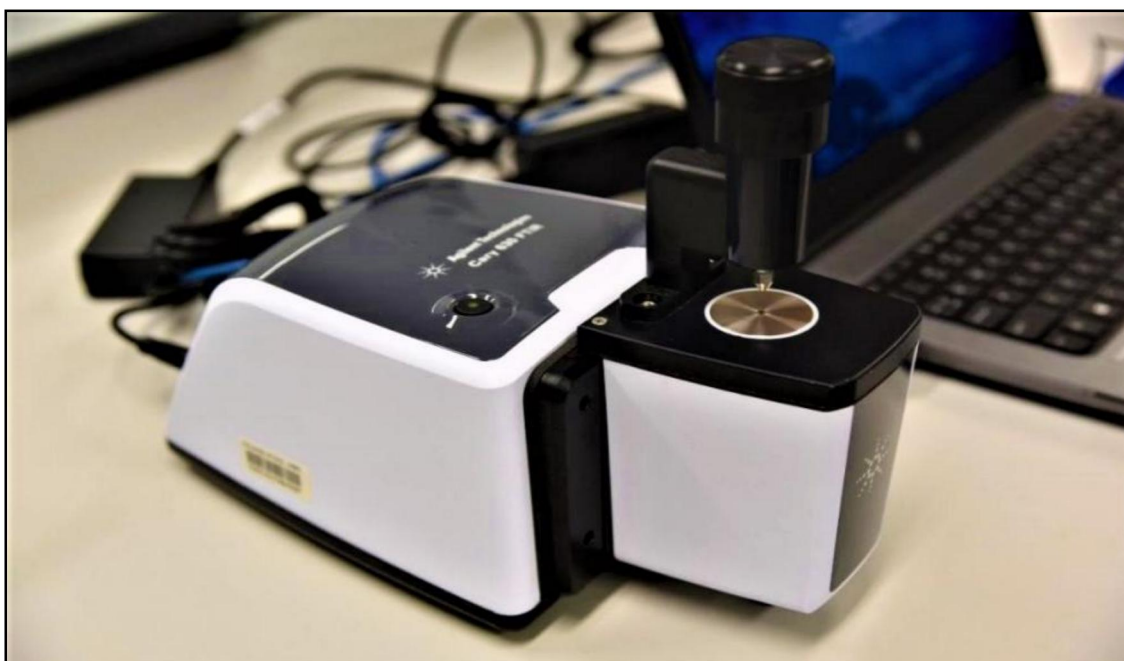
Figure 17 : Fourier transformed infrared spectrometer.

Principle of the infrared spectrophotometer : The IR spectrophotometer comprises an infrared radiation source, an optical grating and a system for splitting the beam into two beams (one for reference, the other for the analysis of the sample), and a photometer for converting the energy received into electrical energy. The photometer is linked to a recorder.

The positions of adsorption bands in an IR spectrum are identified either in wavelength (nm) or in wavenumber n (cm-1). The detection system measures the energy difference between the two beams and emits a signal proportional to this difference. The greater the difference, the more intensity is absorbed.

II.5.3. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals on the surface of solid samples. The resulting electron signals reveal information about the sample, including its external morphology (texture), chemical composition, crystal structure and the orientation of its constituent materials. In most applications, data is collected over a selected area of the sample surface, and a two-dimensional image is produced showing the spatial variations of these properties. Areas from around 1 cm to 5 microns wide can be imaged in a scanning mode using conventional SEM techniques (magnification 20X up to around 30,000X, spatial resolution 50 to 100 nm). SEM is also capable of performing localized spot analysis on the sample; this approach is particularly useful for the qualitative or semi-quantitative determination of chemical compositions (by EDX).

Figure 18 : Scanning electron microscope.

II.5.4. Energy dispersive X-ray spectroscopy (EDX analysis)

Energy dispersive X-ray spectroscopy (or EDX) is an analytical technique that can be coupled with a number of applications, including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Combined with this type of photographic equipment, EDX can provide an elemental analysis of surfaces as small as a nanometer. The impact of the electron beam on the substrate produces X-rays characteristic of the elements present on the substrate. The analysis can be used to determine the composition of individual points, or to map the lateral distribution of elements in the scanned area.

Figure 19 : EDX Detector machine.

II.6. Conclusion

In conclusion, this chapter describes the preparation of zinc oxide nanoparticles (ZnO NPs) using a biosynthesis approach with plant extracts. The raw materials used include Aloe vera plant and zinc sulfate as a precursor for ZnO NPs.

The biosynthesis of ZnO NPs involves the preparation of plant extracts from Aloe vera leaves and gel. The extracts act as reducing agents and stabilizers for the metal precursors. The plant extracts contain phytochemicals that contribute to the reduction process. Factors such as pH, temperature, and contact time affect the synthesis and the stabilization of the nanoparticles. The prepared zinc oxide nanoparticles are then characterized using various techniques. X-ray diffraction (XRD) is used to determine the crystal structure and lattice parameters of the nanoparticles. Fourier transform infrared spectroscopy (FTIR) is employed to identify the chemical groups present in the samples. Scanning electron microscopy (SEM) provides information about the surface morphology and composition of the nanoparticles. Energy dispersive X-ray spectroscopy (EDX) is used for elemental analysis of the nanoparticles. Overall, this chapter provides a detailed description of the preparation and characterization of zinc oxide nanoparticles with a biosynthesis approach using Aloe vera plant extracts whitch offer potential applications in various fields, including materials science, nanotechnology, and biotechnology.

Chapter III :

Results & discussion

III.1. Introduction

In this chapter, we present the results of the characterization of the nanoparticles prepared during this study. As presented in the previous chapter, the zinc oxide nanoparticles were synthesized by the sol-gel route using a green method. The samples obtained were analyzed using the following characterization methods: X-ray diffraction (XRD) to study structural properties, and Fourier transform infrared (FTIR) to determine the nature of the various bonds found in the nanopowders. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to study the morphology and the elementary surface composition.

III.2. Characterization of the zinc oxide powder

III.2.1. Analysis of the zinc oxide powder X-ray spectra

The samples used in our work were taken at room temperature using a X-ray diffractometer at the industrial technology research center (**CRTI**).

The synthesized powders has a phase composition of (**100.0%**) zinc oxide zincite, and an elemental composition by weight % of : **80.3% Zn** and **19.7% O.** The particles have an hexagonal crystalline structure and belong to space group **P 63 mc**. The density is **5.678 g/cm3** and the cell parameters **«a»** and **«c»** are respectively : **a = 3.2493 Å   c = 5.2057 Å**

The crystallite size, D, has been calculated by applying Scherrer's equation as :

$$D = K \lambda / \beta_{hkl} \cos\theta_{hkl}$$

With :

k= 0.95-0.98 shape factor

λ=1.541874 Å (X-ray wavelength)

β_{hkl}= half-width of the diffraction band (FWHM in radians) * 0.017

θ_{hkl}= Bragg-diffraction angle

➢ **Simple 01 :** ZnO NPs synthesised by leaf extract and calcinated at 500°C (4h).
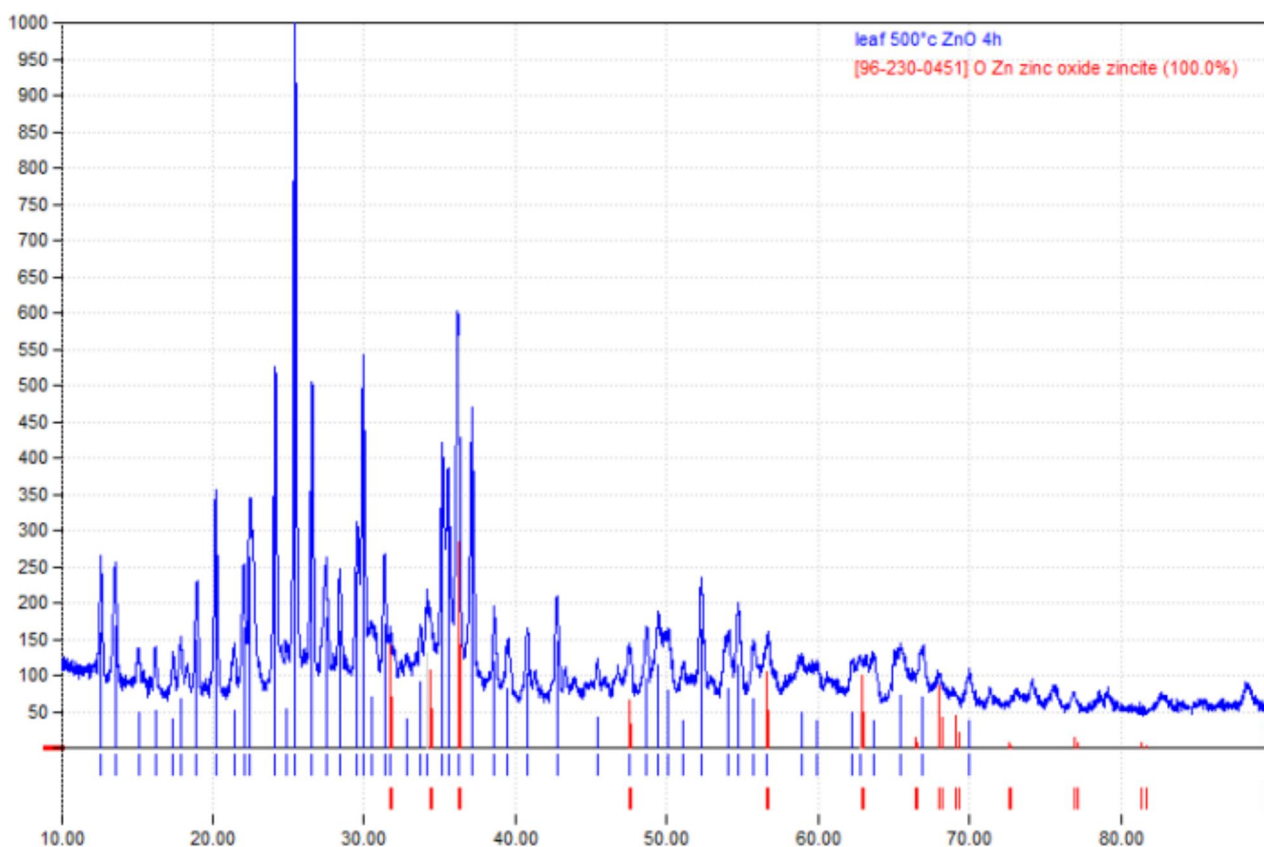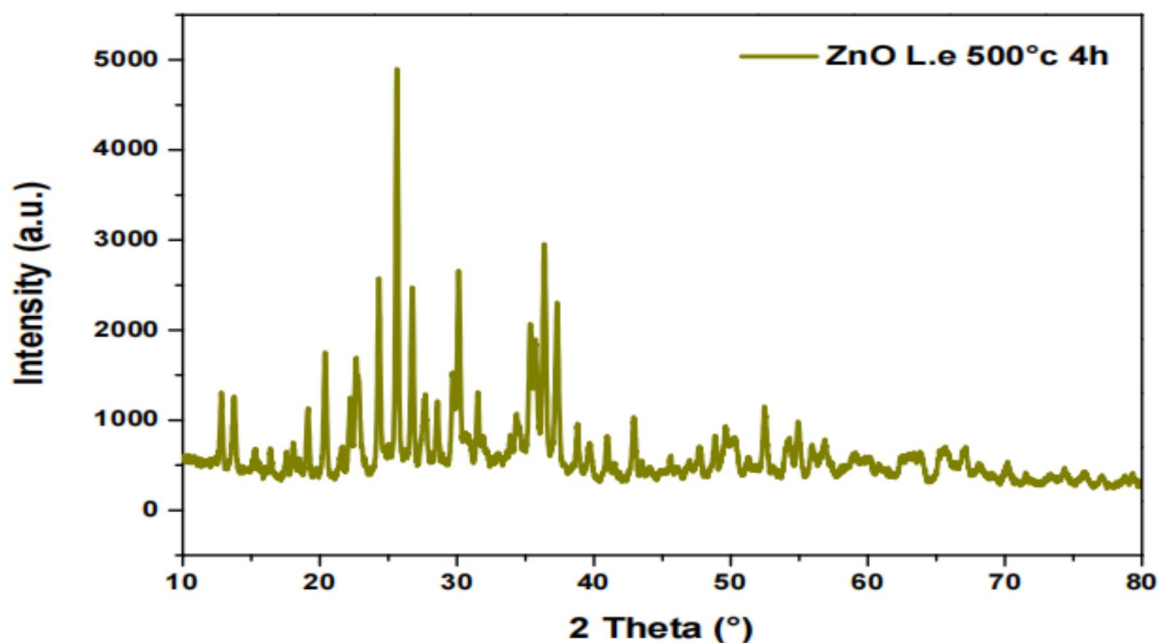
Figure 20 : X-ray diffraction spectrum of ZnO nanoparticles prepared using aqueous Aloe extract and calcined at 500°C for 4h.

<u>**Table 09 :**</u> Peak identification for sample 01.

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
22	31.71	2.8218	65.92	261.15	0.6899
25	34.19	2.6229	131.81	307.16	0.4058
28	36.22	2.4805	568.87	795.42	0.2435
35	47.54	1.9128	67.65	126.12	0.3246
44	56.65	1.6249	81.34	208.50	0.4464
48	62.79	1.4798	49.81	406.28	1.4203

✓ **Interpretation :**   The figure (20) shows the XRD pattern of zinc oxide nanoparticles synthesized using leaf extract and calcinated at 500°C (4h). A total of 58 peaks are observed. The confirmation was done using JCPDS (96-230-0451) value of ZnO NPs. The major peaks observed at 31.71°, 34.19°, 36.22°, 47.54°, 56.65°, and 62.79°. The identification of each peak is shown in table (9). The average particle size calculated using Scherer formula was found to be **Dmoy=35.97 nm.**

➢ **Simple 02 :** ZnO NPs synthesised by leaf extract and calcinated at 400°C (2h).
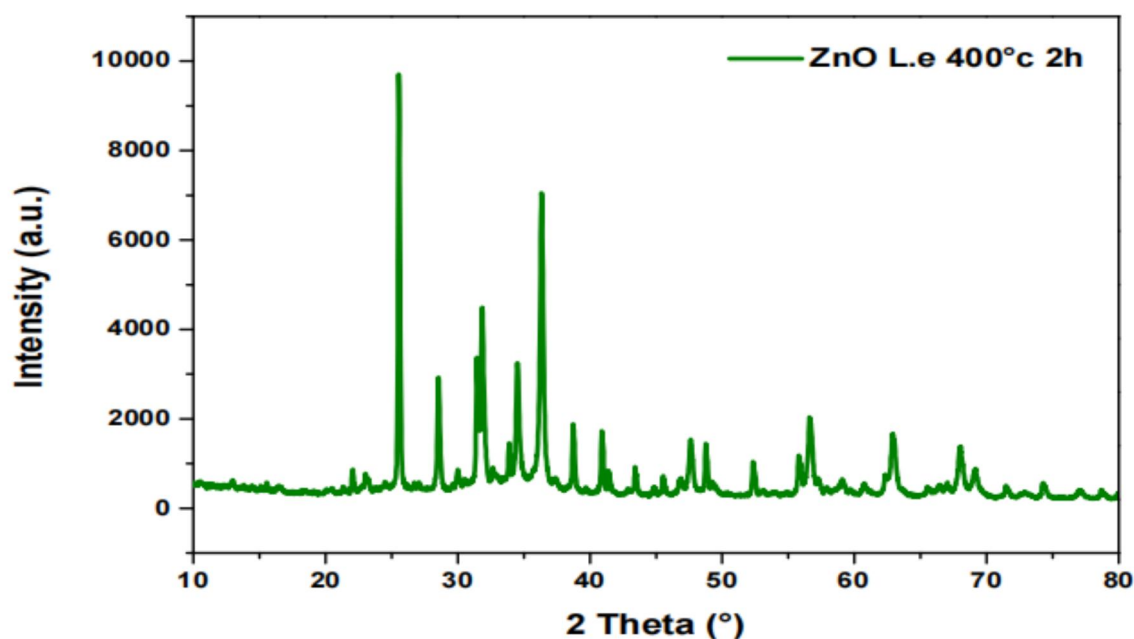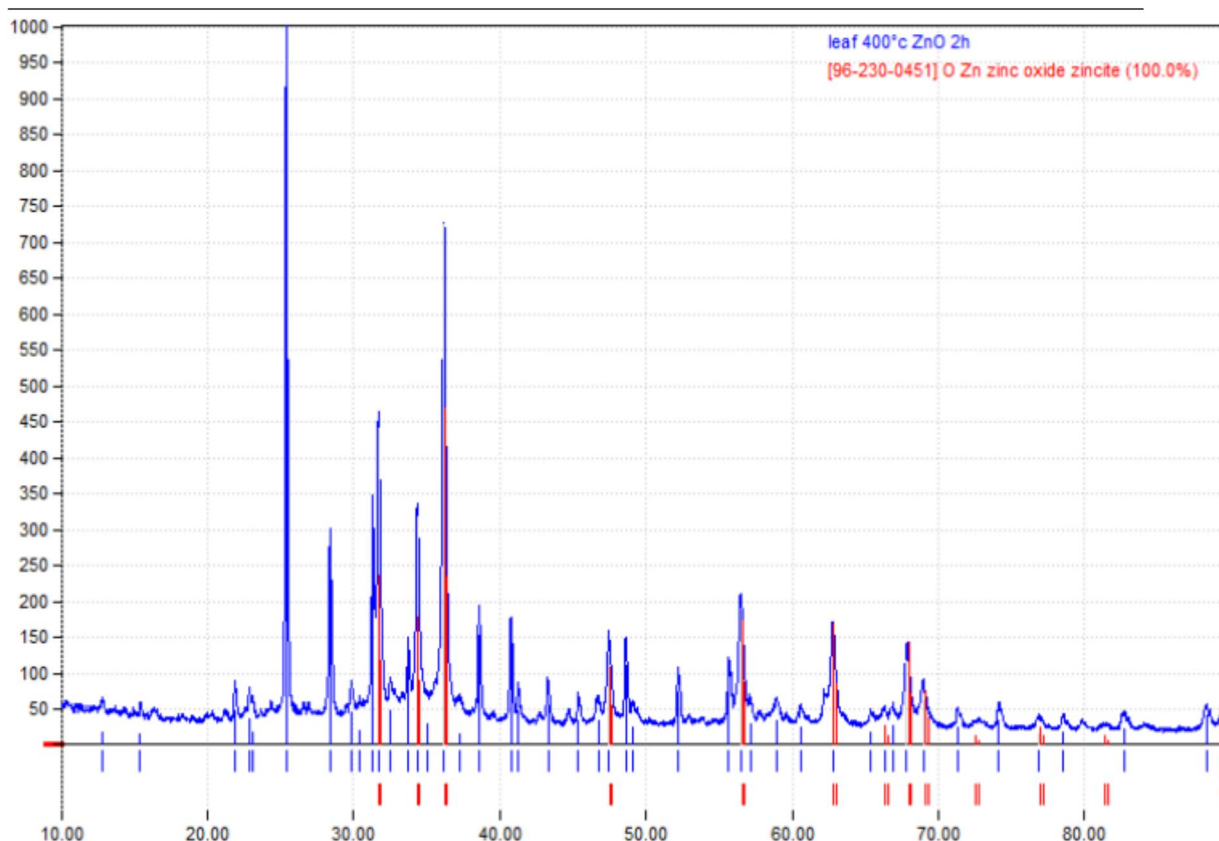
Figure 21 : X-ray diffraction spectrum of ZnO nanoparticles prepared using aqueous Aloe extract and calcined at 400°C for 2h.

Table 10 : Peak identification for sample 02.

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
11	31.71	2.8218	441.07	1486.60	0.2841
14	34.37	2.6094	316.32	913.82	0.2435
16	36.19	2.4819	724.02	2091.65	0.2435
24	47.48	1.9151	124.30	478.80	0.3246
29	56.48	1.6292	187.97	633.53	0.2841
33	62.77	1.4802	147.13	637.59	0.3652
35	66.32	1.4094	22.47	86.56	0.3246
36	66.87	1.3991	25.65	98.81	0.3246
37	67.85	1.3814	117.52	509.28	0.3652
38	68.96	1.3618	60.85	322.27	0.4464
41	76.86	1.2404	15.96	76.82	0.4058
45	89.48	1.0953	15.30	81.03	0.4464

✓ **Interpretation :**   The figure (21) shows the XRD pattern of zinc oxide nanoparticles synthesized using leaf extract and calcinated at 400°C for 2h. A total of 58 peaks are observed. A total of 12 peaks matched. The major peaks observed at 31.71°, 34.37°, 36.19°, 47.48°, 56.48°, and 62.77°. are perfectly indexed to : (100),(002),(101),(102),(110),(103),(200), (112),(201), and (202) lattice planes of hexagonal zincite structure.

✓ The diffraction pattern data obtained were compared with original JCPDS data (96-230-0451) and found good matching value of ZnO NPs [26]. The average size of ZnO particle size calculated using Scherer formula was found to be **D moy = 53.03 nm.**

➢ **Simple 03 :** ZnO NPs synthesised by gel extract and calcinated at 400°C (2h).
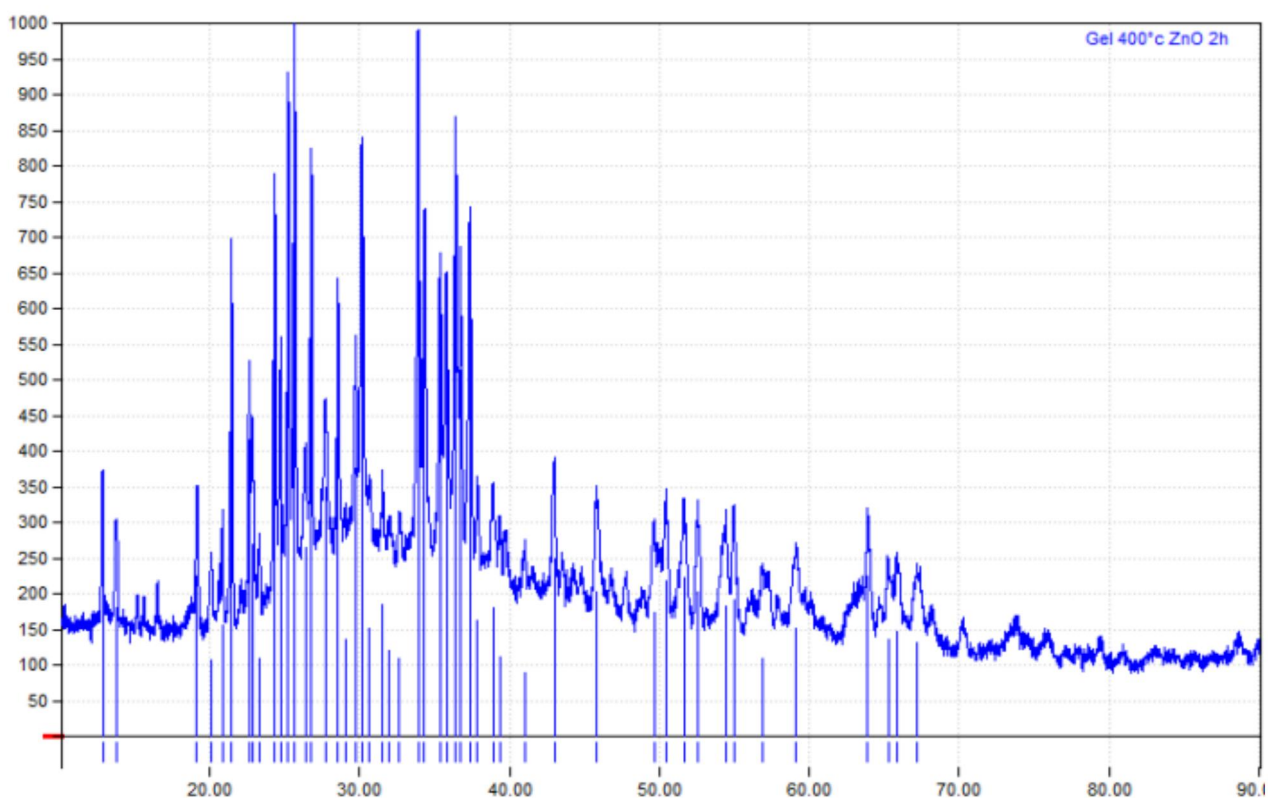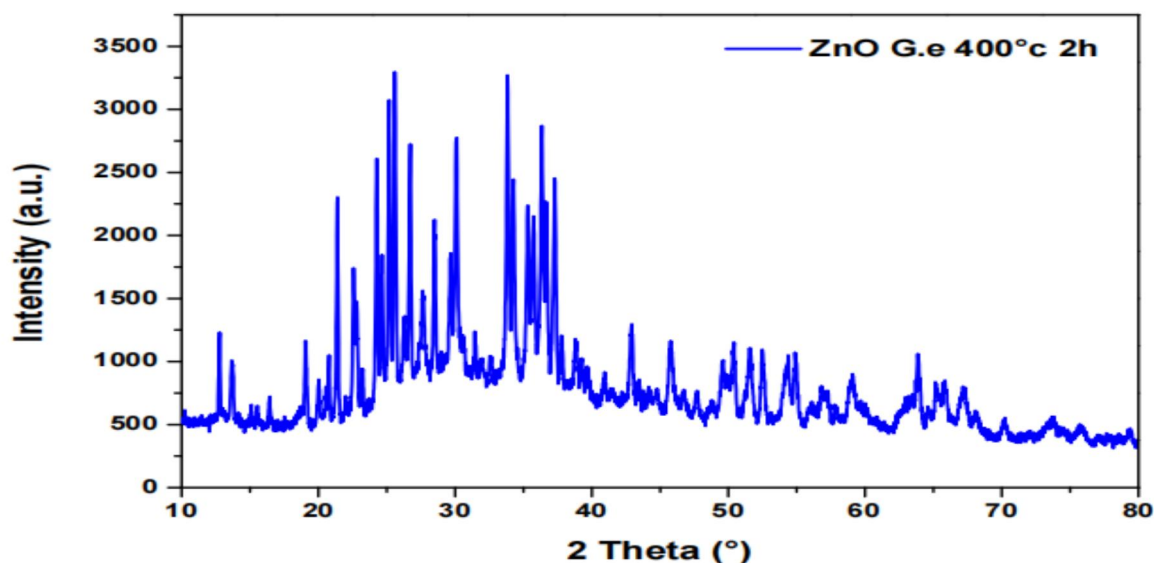
Figure 22 : X-ray diffraction spectrum of ZnO nanoparticles prepared using Aloe gel extract and calcined at 400°C for 2h.
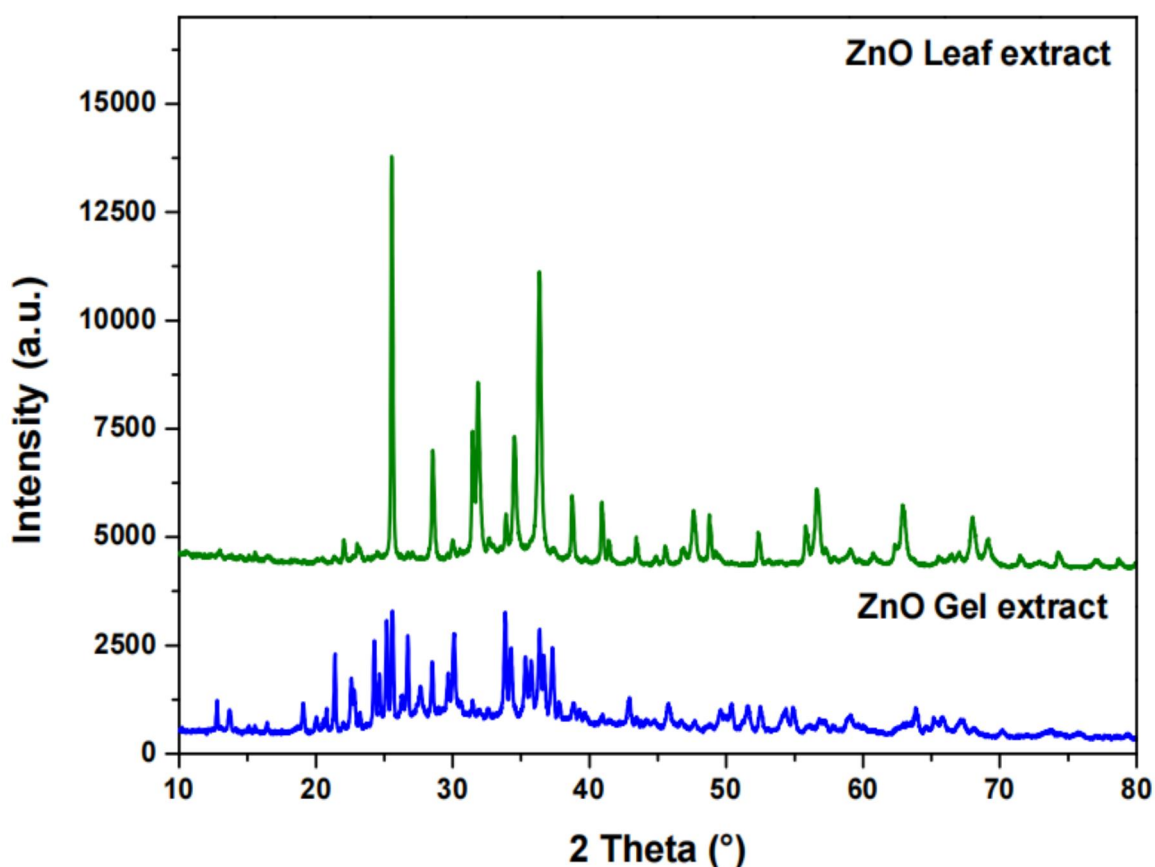
Figure 23 : Comparative spectrum between ZnO nanoparticles synthesized from leaf extract and zinc oxide NPs produced from gel extract.

Table 11 : Peak identification for sample 03.

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
22	31.54	2.8363	186.35	153.80	0.2435
26	34.34	2.6112	634.49	523.66	0.2435
28	35.83	2.5065	537.09	591.03	0.3246

✓ **Interpretation :** The experimental spectrum shown in figure 22 does not match the JCPDS data for ZnO zincite. However, as shown in figure 23, the superposition of the spectrum of ZnO nanoparticles synthesized by leaf extract on the spectrum of zinc oxide NPs elaborated from gel extract, shows a certain correspondence, notably for the three most intense peaks, namely No. : 11, 14 and 16. Table(10).

✓ The spectra shown in figures 20 and 22 reveals peaks of average intensity before the peak at 31.71° which is characteristic of ZnO zincite according to JCPDS data. It is conceivable to attribute these peaks to the minerals present in Aloe Vera.

✓ The minerals identified, as well as the secondary metabolites present in the leafs and Aloe gel extracts, not only stabilize the NPs but also reduce the phenomenon of agglomeration.These compounds offer significant reactivity to NPs synthesized by biogenic route compared with those synthesized by pyisico-chemical methods, and that's what makes our study so worthwhile.

III.2.2. Analysis of infrared spectra of zinc oxide powder and plant extracts

FTIR analyses were carried out using a Cary 630 FTIR Spectrometer with ATR sampling module (figure). The limits of the adsorption bands were set between 500 and 4000 cm-1.
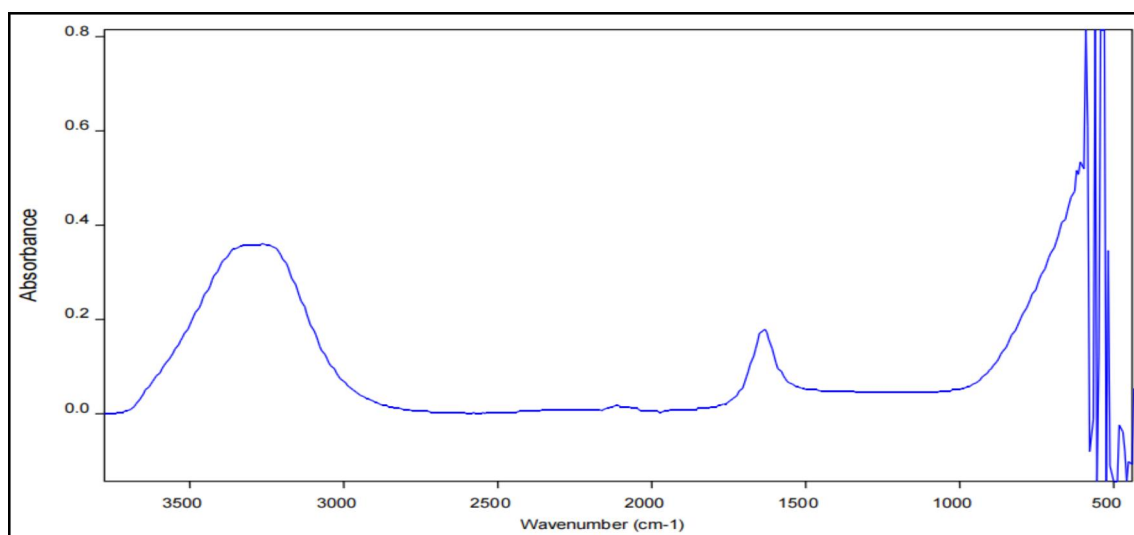
Figure 24 : Leaf extract infrared spectra.
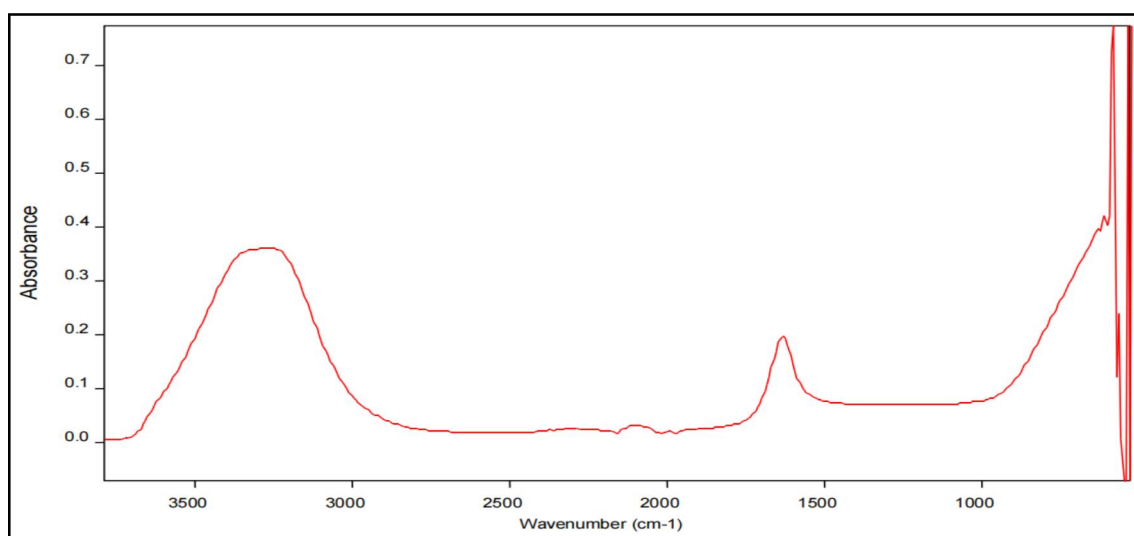
Figure 25 : Gel extract infrared sepectra.
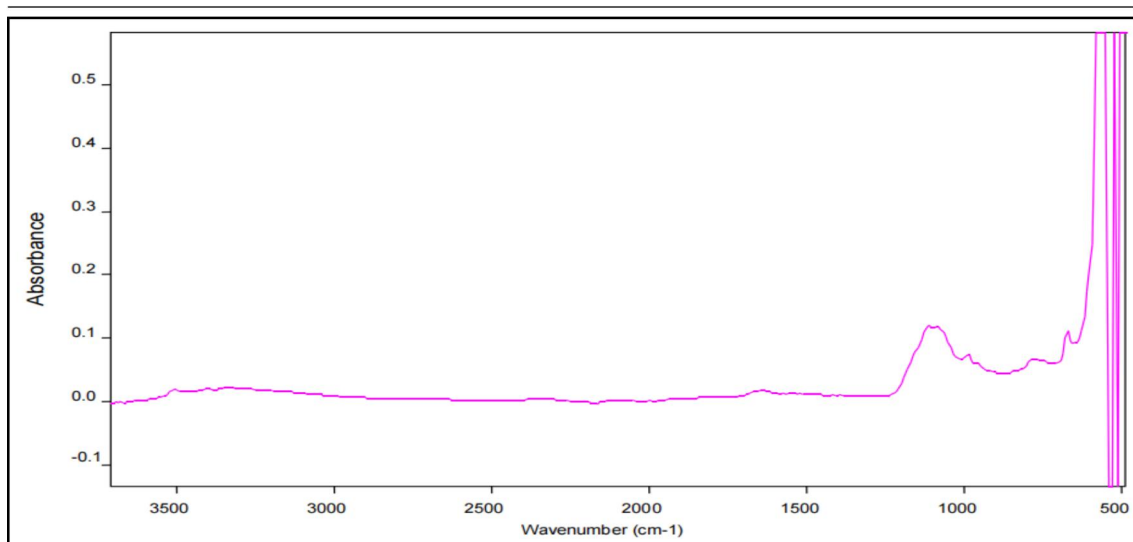
Figure 26 : Spectrum of zinc oxide nanoparticles synthesized by leaf extract.
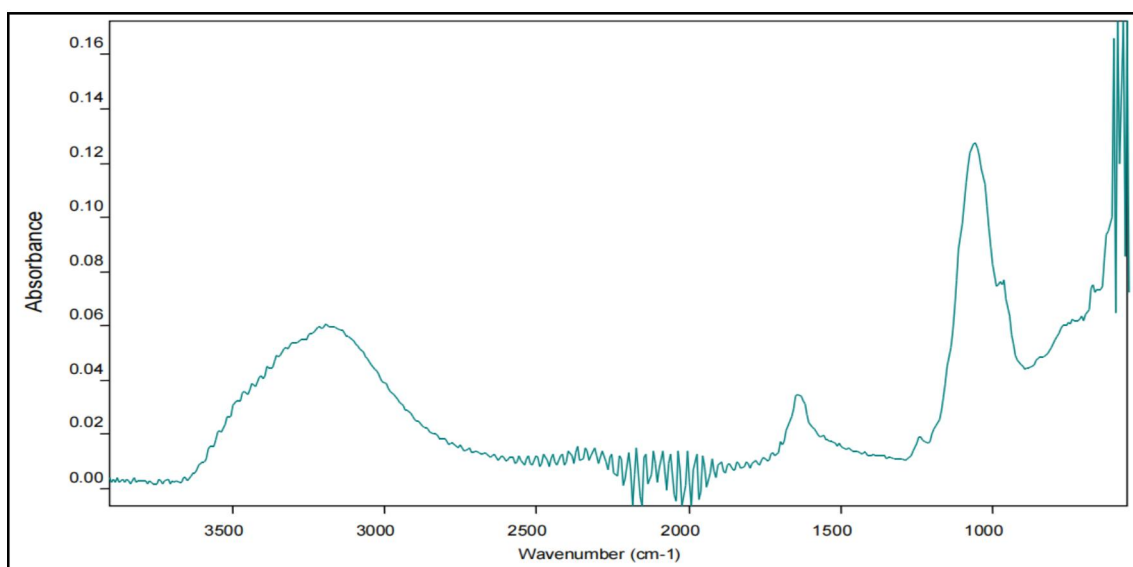
Figure 27 : Spectrum of zinc oxide nanoparticles synthesized by gel extract.

✓ **Interpretation :** FTIR studies were conducted to verify the presence of the functional groups in the aquous extract. As illustrated in Fig (23,24) data in the range from 2800–3500 cm-1, shows a peak due to the presence of the hydroxyl functional group at around 3300 cm-1 for both the Aloe Vera leaves and gel extracts. Carbonyl groups, including the ester estate functional groups (CAOAC), were observed at around 1050 cm-1 for both the plant extract. Additional peaks were observed from FTIR spectrum in the range from 1220–1600 cm-1 , corresponding to the CAO bond at around 1250 cm-1, and at around 1380 cm-1 corresponding to the methyl (CH3) functional group.

✓   Stronger peaks were observed in these ranges for the the Aloe Vera extract. These results indicate the presence of anthocyanin and chlorophyll molecules various cinnamic acids and their derivatives, anthracene compounds, and flavonoids, some of which have been reported previously in Aloe species, miller leaf extract. The high intensity band around 440 cm-1 is due to stretching mode of zinc and oxygen bond .Thus, our result concurs with the observations indicating the role of phenolic compounds, terpenoids and proteins in synthesis and stability of ZnONPs. Proteins are known to form a corona around NPs, making them more dispersible and prevent agglomeration in aqueous medium. Furthermore, the free amino and carboxylic groups interaction with zinc surface, reportedly contributes for stability of ZnONP.

✓

III.2.3. SEM and EDX Analysis of zinc oxide nanoparticles
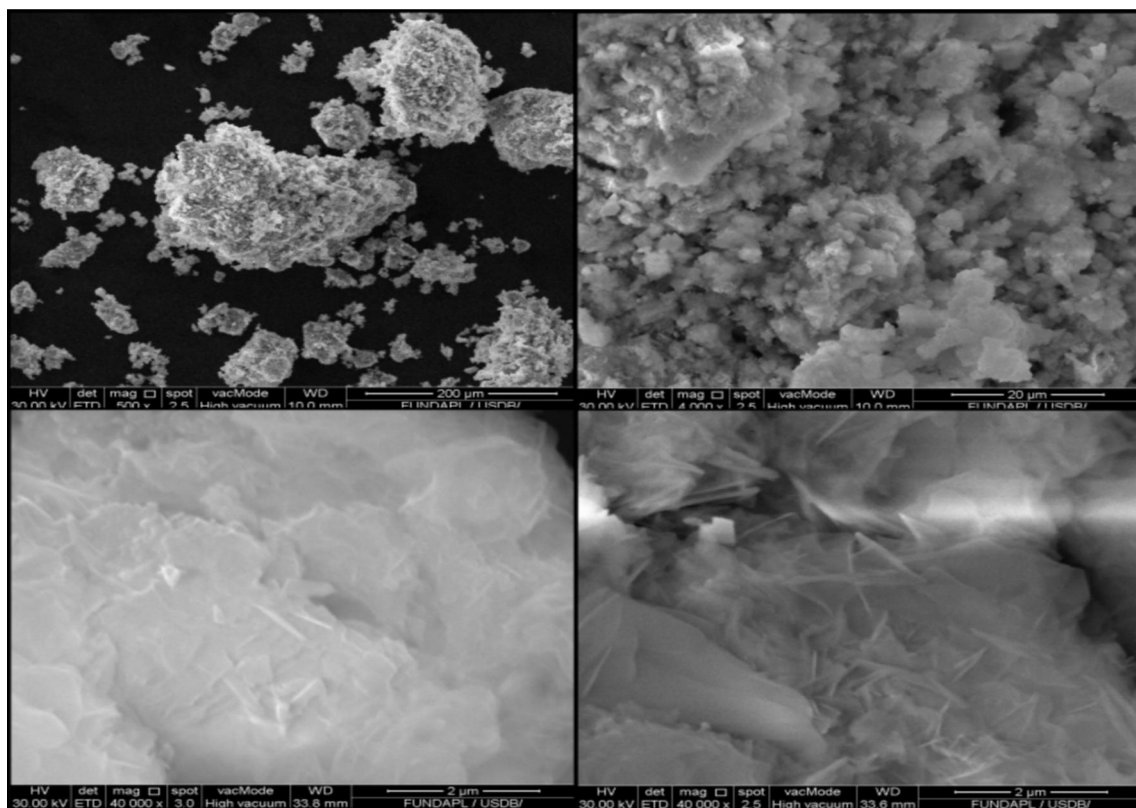
Figure 28 : Scanning electron microscopy SEM images.

✓ **Interpretation :** The SEM images Figure (27) at 40,000 X magnification exhibited pleomorphic ZnONPs. The elemental composition of ZnONPs was analyzed through EDX, and found comprised of zinc, oxygen, and other minerals for the aqueous extract of plant Figure (28). The Results indicate two emission peaks of metallic zinc and a small peaks of oxygen, which confirmed the formation of ZnONPs. Furthermore, the image exhibited ZnONPs of different shapes as ZnO nanosheets with well-defined particle boundary and nanowires in nanometric size with an agglomeration of the particles [27].
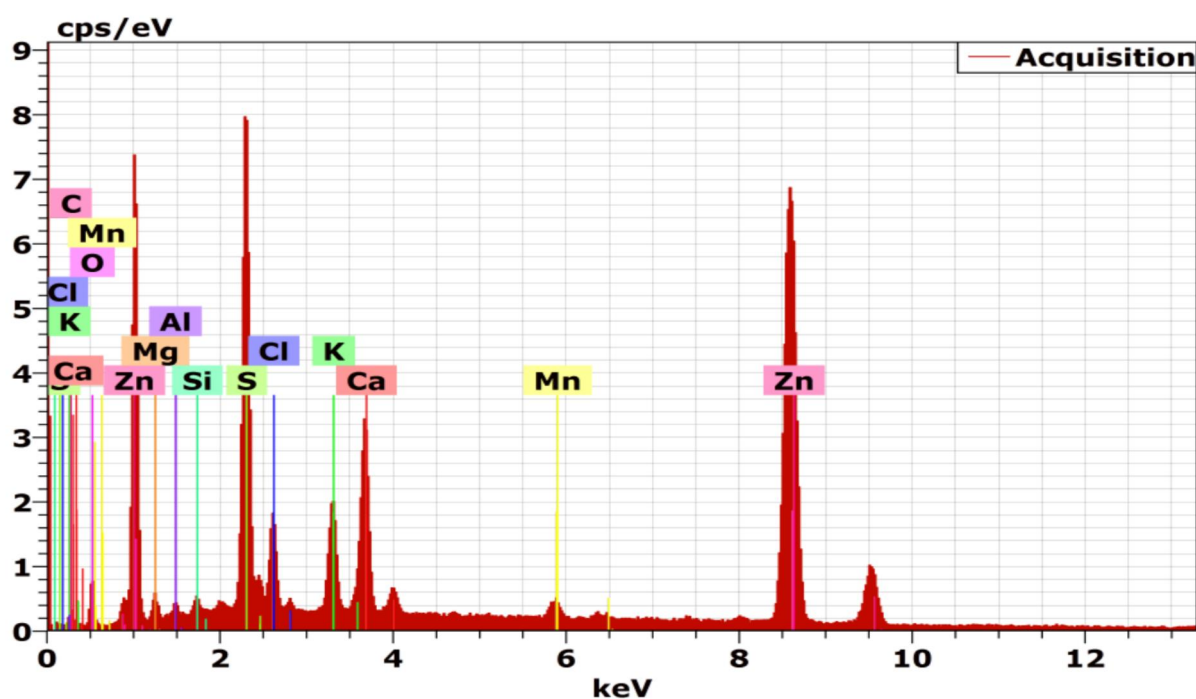
Element	Series	Net unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error.	(3 Sigma) [wt.%]
Zinc	K-series	36740	38.54	51.52	29.44	2.97
Sulfur	K-series	23227	11.91	15.92	18.55	1.43
calcium	K-series	10954	5.82	7.78	7.26	0.62
Potassium	K-series	6456	3.09	4.13	3.95	0.39
Chlorine	K-series	4783	2.65	3.55	3.74	0.39
Oxygen	K-series	1278	6.99	9.34	21.81	4.51
Manganese	K-series	1278	0.75	1.00	0.68	0.16
Magnesium	K-series	935	1.74	2.33	3.58	0.47
Silicon	K-series	675	0.55	0.73	0.97	0.19
aluminium	K-series	544	0.64	0.85	1.18	0.22
carbon	K-series	153	2.13	2.84	8.84	2.77
Total			74.79	100.00	100.00	

Figure 29 : Elemental composition analysis by energy dispersive X-ray spectroscopy.

III.3. Conclusion

In conclusion, the characterization of the zinc oxide nanoparticles (ZnO NPs) synthesized using Aloe vera plant extracts has provided valuable insights into their structural and morphological properties. The X-ray diffraction (XRD) analysis confirmed that the synthesized ZnO NPs exhibited a hexagonal crystalline structure, belonging to space group P 63 mc. The major peaks observed in the XRD patterns matched well with the characteristic peaks of zincite (ZnO) phase. The calculated average particle sizes using Scherrer's equation were found to be 35.97 nm for ZnO NPs synthesized with leaf extract and calcined at 500°C for 4 hours, and 53.03 nm for ZnO NPs synthesized with leaf extract and calcined at 400°C for 2 hours. These results indicate the formation of well-crystallized ZnO NPs.

The Fourier transform infrared spectroscopy (FTIR) analysis provided information about the functional groups present in the Aloe vera plant extracts and the synthesized ZnO NPs. The presence of hydroxyl groups, carbonyl groups, and various organic functional groups was observed in the FTIR spectra of the plant extracts. The FTIR spectrum of the synthesized ZnO NPs showed characteristic peaks corresponding to Zn-O bonding, confirming the formation of zinc oxide nanoparticles. The scanning electron microscopy (SEM) analysis revealed the pleomorphic nature of the ZnO NPs synthesized with Aloe vera plant extracts. The images exhibited ZnO nanosheets with well-defined particle boundaries and nanowires of various shapes, indicating the agglomeration of particles. The energy dispersive X-ray spectroscopy (EDX) analysis confirmed the elemental composition of zinc, oxygen, and other minerals in the synthesized ZnO NPs.

Overall, the characterization results demonstrate the successful synthesis of well-crystallized ZnO nanoparticles using Aloe vera plant extracts. The obtained structural and morphological information provides a foundation for further understanding and potential applications of these nanoparticles in various fields.

Genral conclusion

In conclusion, this study focused on the preparation and characterization of zinc oxide nanoparticles (ZnO NPs) using the biosynthesis approach with Aloe vera plant extracts.

The method allowed for the controlled synthesis of ZnO NPs under mild conditions, resulting in high purity and well-defined crystalline structures. The advantages of this method include low synthesis temperature, control over nanoparticle morphology, and the use of molecular precursors in solution, leading to homogeneity in the final product. On the other hand, using Aloe vera plant extracts provided a green and sustainable method for ZnO NP synthesis. The plant extracts acted as reducing agents and stabilizers, effectively converting the metal precursors into nanoparticles. This approach capitalized on the phytochemicals present in the plant extracts, which not only facilitated the reduction process but also contributed to the stability of the nanoparticles.

The characterization techniques employed, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX), provided valuable insights into the structural, compositional, and morphological properties of the synthesized ZnO NPs. XRD confirmed the crystalline nature of the nanoparticles and provided information about their crystal structure. FTIR analysis identified the functional groups present in the plant extracts and confirmed the formation of ZnO NPs. SEM imaging revealed the morphology and particle size of the nanoparticles, while EDX analysis confirmed their elemental composition. Overall, this study demonstrated the successful synthesis of ZnO NPs using a green approache. The findings contribute to the understanding of ZnO nanoparticle synthesis and highlight the potential of Aloe vera plant extracts as a sustainable and ecologic method for nanoparticle production. The characterized ZnO NPs can find applications in various fields such as materials science, nanotechnology, and biotechnology, including but not limited to catalysis, sensors, photovoltaics, and antimicrobial agents.

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Match! Phase Analysis Report

Sample: leaf 500°c ZnO 4h

Sample Data

File name	leaf 500°c ZnO 4h.dat
File path	C:/Users/Snow/Desktop/DRX
Data collected	juin 28, 2023 10:42:30
Data range	9.818° - 89.821°
Original data range	9.998° - 90.001°
Number of points	3944
Step size	0.020
Rietveld refinement converged	No
Alpha2 subtracted	No
Background subtr.	No
Data smoothed	No
2theta correction	-0.18°
Radiation	X-rays
Wavelength	1.541874 Å
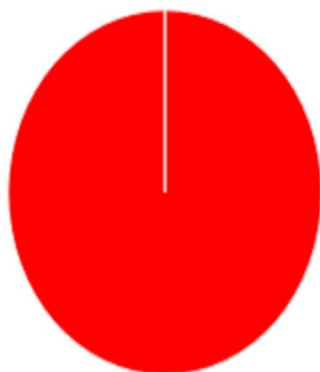
Analysis Results

Phase composition (Weight %)

zinc oxide zincite (100.0%)

Elemental composition (Weight %)
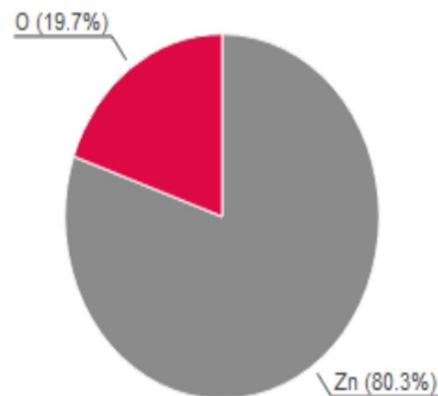
O (19.7%)

Zn (80.3%)

Index	Amount (%)	Name	Formula sum	Element	Amount (weight %)
A	100.0	zinc oxide zincite	O Zn	Zn	80.3%
	32.3	Unidentified peak area		O	19.7%(*)
				*LE (sum)	19.7%

Details of identified phases

A: zinc oxide zincite (100.0 %)*

Formula sum	O Zn
Entry number	96-230-0451
Figure-of-Merit (FoM)	0.630727*
Total number of peaks	58
Peaks in range	58
Peaks matched	11
Intensity scale factor	0.28*
Space group	P 63 m c
Crystal system	hexagonal
Unit cell	a= 3.2493 Å c= 5.2057 Å
I/Ic	6.77
Calc. density	5.678 g/cm³

Reference   Schreyer Martin, Guo Liangfeng, Thirunahari Satyanarayana, Gao Feng, Garland Marc, "Simultaneous determination of several crystal structures from powdermixtures: the combination of powder X-ray diffraction, band-targetentropy minimization and Rietveld methods", Journal of Applied Crystallography **47(2)**, 659-667 (2014)

(*)2theta values have been shifted internally for the calculation of the amounts, the intensity scaling factors as well as the figure-of-merit (FoM), due to the active search-match option 'Automatic zero point adaption'.

Search-Match

Settings

Reference database used	COD-Inorg 2022.11.07
Automatic zeropoint adaptation	Yes
Downgrade entries with low scaling factors	Yes
Minimum figure-of-merit (FoM)	0.60
2theta window for peak corr.	0.30 deg.
Minimum rel. int. for peak corr.	0
Parameter/influence 2theta	0.50
Parameter/influence intensities	0.50
Parameter multiple/single phase(s)	0.50

Selection Criteria

Elements:

Elements that must be present:	O, Zn
Elements that must NOT be present:	All elements not mentioned above
Element count:	2

Compound:

Name:	zinc oxide
Formula sum:	O Zn

Peak List

No.	2theta [º]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM	Matched
1	12.64	7.0044	158.37	221.45	0.2435	
2	13.57	6.5247	167.46	273.17	0.2841	
3	15.09	5.8701	48.99	57.08	0.2029	
4	16.23	5.4616	52.27	48.72	0.1623	
5	17.39	5.1008	41.24	48.05	0.2029	
6	17.89	4.9574	68.09	95.21	0.2435	
7	18.95	4.6836	150.97	175.91	0.2029	
8	20.21	4.3948	276.69	386.87	0.2435	
9	21.42	4.1477	51.73	60.28	0.2029	
10	22.05	4.0308	166.77	272.04	0.2841	
11	22.48	3.9554	263.59	491.41	0.3246	
12	24.14	3.6864	467.99	654.37	0.2435	
13	24.87	3.5798	54.02	75.54	0.2435	
14	25.44	3.5011	1000.00	1398.24	0.2435	
15	26.58	3.3540	452.40	632.57	0.2435	
16	27.49	3.2446	179.95	335.48	0.3246	
17	28.40	3.1424	162.66	189.53	0.2029	
18	29.56	3.0220	243.04	453.11	0.3246	
19	29.95	2.9840	465.30	759.03	0.2841	
20	30.45	2.9354	71.89	368.56	0.8928	
21	31.35	2.8538	171.18	239.35	0.2435	
22	31.71	2.8218	65.92	261.15	0.6899	A
23	32.85	2.7267	40.35	122.23	0.5275	
24	33.74	2.6566	90.85	169.37	0.3246	
25	34.19	2.6229	131.81	307.16	0.4058	A
26	35.18	2.5510	374.01	610.12	0.2841	
27	35.57	2.5243	305.25	640.21	0.3652	
28	36.22	2.4805	568.87	795.42	0.2435	A
29	37.13	2.4216	417.21	680.58	0.2841	
30	38.63	2.3308	120.54	140.46	0.2029	
31	39.50	2.2813	81.81	152.52	0.3246	
32	40.80	2.2117	104.48	146.09	0.2435	
33	42.75	2.1153	146.53	239.03	0.2841	
34	45.41	1.9975	42.09	39.23	0.1623	
35	47.54	1.9128	67.65	126.12	0.3246	A
36	48.67	1.8708	96.93	180.72	0.3246	
37	49.44	1.8434	115.34	322.55	0.4870	
38	50.09	1.8210	81.34	227.45	0.4870	
39	51.09	1.7879	38.71	63.14	0.2841	
40	52.28	1.7497	162.97	265.85	0.2841	
41	54.05	1.6967	83.10	271.11	0.5681	
42	54.72	1.6775	116.16	216.57	0.3246	
43	55.73	1.6493	69.46	145.69	0.3652	
44	56.65	1.6249	81.34	208.50	0.4464	A
45	58.88	1.5685	51.06	226.07	0.7710	
46	59.95	1.5429	39.47	91.99	0.4058	
47	62.27	1.4911	49.21	103.20	0.3652	
48	62.79	1.4798	49.81	406.28	1.4203	A

49	63.67	1.4616	39.25	100.62	0.4464
50	65.47	1.4256	72.35	303.49	0.7304
51	66.93	1.3980	70.29	147.42	0.3652
52	70.00	1.3441	38.27	71.35	0.3246

Integrated Profile Areas

Based on calculated profile

Profile area	*Counts*	*Amount*
Overall diffraction profile	2221385	100.00%
Background radiation	1414595	63.68%
Diffraction peaks	806791	36.32%
Peak area belonging to selected phases	89967	4.05%
Peak area of phase A (zinc oxide zincite)	*89967*	*4.05%*
Unidentified peak area	716823	32.27%

Peak Residuals

Peak data	*Counts*	*Amount*
Overall peak intensity	15018	100.00%
Peak intensity belonging to selected phases	10906	72.62%
Unidentified peak intensity	4111	27.38%

Diffraction Pattern Graphics

leaf 500°c ZnO 4h
[96-230-0451] O Zn zinc oxide zincite (100.0%)
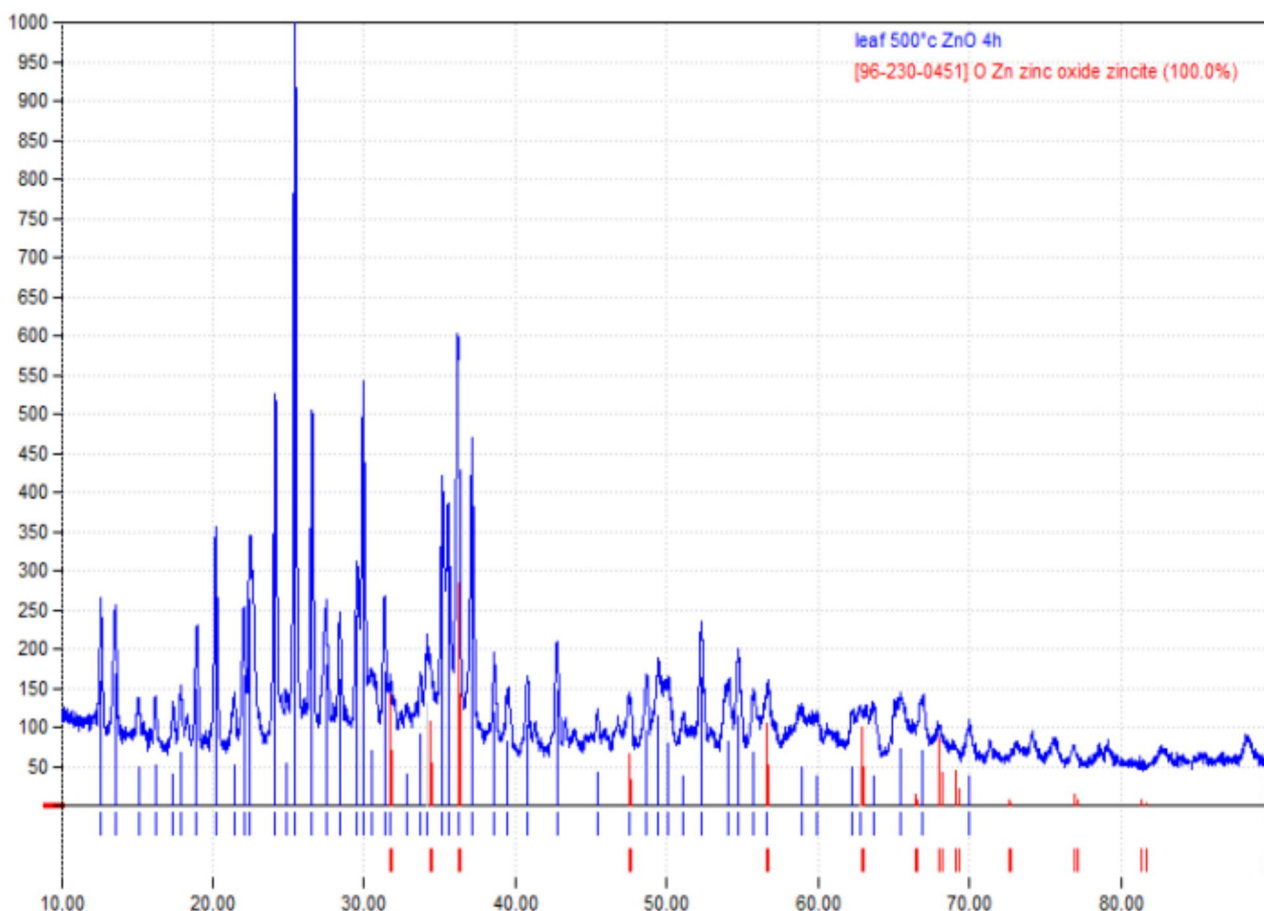
Match! Phase Analysis Report

Sample: leaf 400°c ZnO 2h

Sample Data

File name	leaf 400°c ZnO 2h.dat
File path	C:/Users/Snow/Desktop/DRX
Data collected	juin 28, 2023 10:42:30
Data range	9.858° - 89.861°
Original data range	9.998° - 90.001°
Number of points	3944
Step size	0.020
Rietveld refinement converged	No
Alpha2 subtracted	No
Background subtr.	No
Data smoothed	No
2theta correction	-0.14°
Radiation	X-rays
Wavelength	1.541874 Å
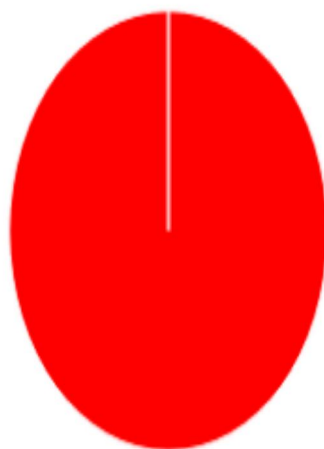
Analysis Results

Phase composition (Weight %)

zinc oxide zincite (100.0%)

Elemental composition (Weight %)
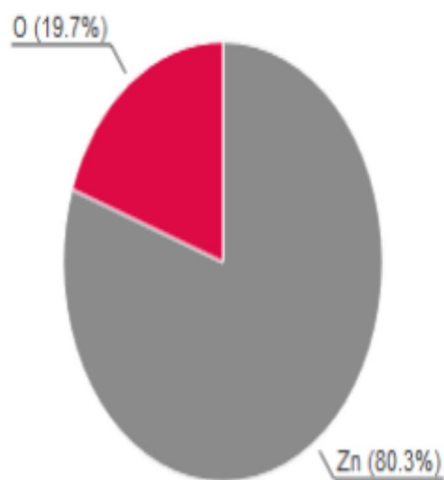
O (19.7%)

Zn (80.3%)

Index	Amount (%)	Name	Formula sum		Element	Amount (weight %)
A	100.0	zinc oxide zincite	O Zn		Zn	80.3%
	30.5	*Unidentified peak area*			O	19.7%(*)
					LE (sum)	19.7%

Details of identified phases

A: zinc oxide zincite (100.0 %)*

Formula sum	O Zn
Entry number	96-230-0451
Figure-of-Merit (FoM)	0.782721*
Total number of peaks	58
Peaks in range	25
Peaks matched	18
Intensity scale factor	0.47*
Space group	P 63 m c
Crystal system	hexagonal
Unit cell	a= 3.2493 Å c= 5.2057 Å
I/Ic	6.77
Calc. density	5.678 g/cm³

Reference* Schreyer Martin, Guo Liangfeng, Thirunahari Satyanarayana, Gao Feng, Garland Marc, "Simultaneous determination of several crystal structures from powdermixtures: the combination of powder X-ray diffraction, band-targetentropy minimization and Rietveld methods", Journal of Applied Crystallography **47(2)**, 659-667 (2014)

(*)2theta values have been shifted internally for the calculation of the amounts, the intensity scaling factors as well as the figure-of-merit (FoM), due to the active search-match option 'Automatic zero point adaption'.

Search-Match

Settings

Reference database used	COD-Inorg 2022.11.07
Automatic zeropoint adaptation	Yes
Downgrade entries with low scaling factors	Yes
Minimum figure-of-merit (FoM)	0.60
2theta window for peak corr.	0.30 deg.
Minimum rel. int. for peak corr.	0
Parameter/influence 2theta	0.50
Parameter/influence intensities	0.50
Parameter multiple/single phase(s)	0.50

Selection Criteria

Elements:

Elements that must be present:	O, Zn
Elements that must NOT be present:	All elements not mentioned above
Element count:	2

Compound:

Name:	zinc oxide

Peak List

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM	Matched
1	12.82	6.9054	17.78	25.68	0.1217	
2	15.42	5.7475	15.27	14.70	0.0812	
3	21.91	4.0567	47.92	92.29	0.1623	
4	22.88	3.8863	36.67	70.62	0.1623	
5	23.09	3.8526	18.37	53.06	0.2435	
6	25.42	3.5040	1000.00	1925.96	0.1623	
7	28.40	3.1424	271.38	653.33	0.2029	
8	29.86	2.9920	45.67	153.93	0.2841	
9	30.39	2.9412	19.32	55.81	0.2435	
10	31.32	2.8557	309.22	595.54	0.1623	
11	31.71	2.8218	441.07	1486.60	0.2841	A
12	32.52	2.7532	47.34	205.16	0.3652	
13	33.76	2.6551	110.75	266.63	0.2029	
14	34.37	2.6094	316.32	913.82	0.2435	A
15	35.10	2.5568	29.13	1304.33	3.7739	
16	36.19	2.4819	724.02	2091.65	0.2435	A
17	37.27	2.4127	15.76	68.31	0.3652	
18	38.61	2.3320	152.63	293.95	0.1623	
19	40.78	2.2128	142.08	273.64	0.1623	
20	41.27	2.1878	47.22	90.95	0.1623	
21	43.30	2.0898	54.26	104.51	0.1623	
22	45.39	1.9983	33.87	65.23	0.1623	
23	46.74	1.9433	33.98	147.25	0.3652	
24	47.48	1.9151	124.30	478.80	0.3246	A
25	48.63	1.8723	110.76	159.99	0.1217	
26	49.08	1.8563	24.23	46.66	0.1623	
27	52.20	1.7523	72.58	139.79	0.1623	
28	55.67	1.6510	92.26	222.11	0.2029	
29	56.48	1.6292	187.97	633.53	0.2841	A
30	57.13	1.6122	29.77	172.00	0.4870	
31	58.94	1.5671	33.46	161.08	0.4058	
32	60.60	1.5280	23.77	68.68	0.2435	
33	62.77	1.4802	147.13	637.59	0.3652	A
34	65.37	1.4276	18.23	35.12	0.1623	
35	66.32	1.4094	22.47	86.56	0.3246	A
36	66.87	1.3991	25.65	98.81	0.3246	
37	67.85	1.3814	117.52	509.28	0.3652	A
38	68.96	1.3618	60.85	322.27	0.4464	A
39	71.34	1.3222	25.16	72.68	0.2435	
40	74.14	1.2790	32.99	95.31	0.2435	
41	76.86	1.2404	15.96	76.82	0.4058	A
42	78.54	1.2180	17.78	51.36	0.2435	
43	82.72	1.1667	21.88	84.27	0.3246	
44	88.32	1.1066	40.65	254.46	0.5275	
45	89.48	1.0953	15.30	81.03	0.4464	A

Integrated Profile Areas

Based on calculated profile

Profile area	Counts	Amount
Overall diffraction profile	2117444	100.00%
Background radiation	1232217	58.19%
Diffraction peaks	885227	41.81%
Peak area belonging to selected phases	238982	11.29%
Peak area of phase A (zinc oxide zincite)	*238982*	*11.29%*
Unidentified peak area	646245	30.52%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	15441	100.00%
Peak intensity belonging to selected phases	13573	87.90%
Unidentified peak intensity	1868	12.10%

Diffraction Pattern Graphics

leaf 400°c ZnO 2h
[96-230-0451] O Zn zinc oxide zincite (100.0%)
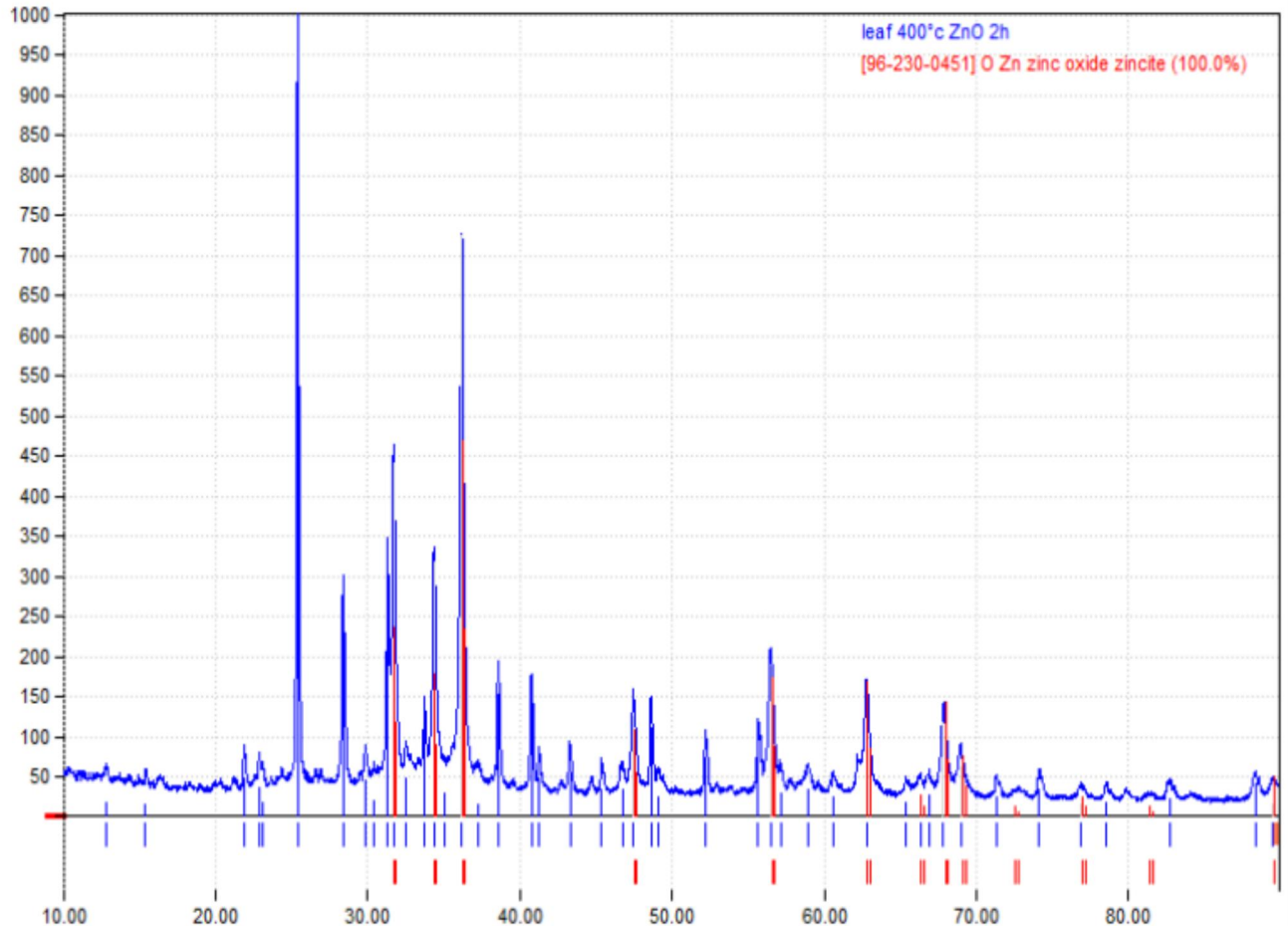
Match! Phase Analysis Report

Sample: Gel 400°c ZnO 2h

Sample Data

File name	Gel 400°c ZnO 2h.dat
File path	C:/Users/Snow/Desktop/DRX
Data collected	juin 28, 2023 10:42:30
Data range	10.078° - 90.081°
Original data range	9.998° - 90.001°
Number of points	3944
Step size	0.020
Rietveld refinement converged	No
Alpha2 subtracted	No
Background subtr.	No
Data smoothed	No
2theta correction	0.08°
Radiation	X-rays
Wavelength	1.541874 Å

Search-Match

Settings

Reference database used	COD-Inorg 2022.11.07
Automatic zeropoint adaptation	Yes
Downgrade entries with low scaling factors	Yes
Minimum figure-of-merit (FoM)	0.60
2theta window for peak corr.	0.30 deg.
Minimum rel. int. for peak corr.	0
Parameter/influence 2theta	0.50
Parameter/influence intensities	0.50
Parameter multiple/single phase(s)	0.50

Selection Criteria

Elements:

Elements that must be present: O, Zn

Elements that must NOT be present: All elements not mentioned above

Peak List

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
1	12.86	6.8854	222.29	91.73	0.1217
2	13.77	6.4308	180.53	124.16	0.2029
3	19.15	4.6354	225.51	124.08	0.1623
4	20.10	4.4176	107.26	59.01	0.1623
5	20.85	4.2602	156.65	64.64	0.1217
6	21.48	4.1368	584.07	321.36	0.1623
7	22.68	3.9211	416.93	229.40	0.1623
8	22.88	3.8868	269.47	222.40	0.2435
9	23.31	3.8167	111.03	61.09	0.1623
10	24.36	3.6537	730.66	402.02	0.1623
11	24.73	3.6006	431.69	237.52	0.1623
12	25.25	3.5266	879.79	605.09	0.2029
13	25.68	3.4690	1000.00	687.77	0.2029
14	26.37	3.3798	266.50	293.26	0.3246
15	26.80	3.3270	726.90	499.94	0.2029
16	27.73	3.2171	350.19	578.05	0.4870
17	28.58	3.1231	533.29	440.14	0.2435
18	29.05	3.0740	136.17	749.20	1.6232
19	29.76	3.0022	375.67	361.72	0.2841
20	30.16	2.9628	755.96	623.91	0.2435
21	30.67	2.9149	153.26	189.73	0.3652
22	31.54	2.8363	186.35	153.80	0.2435
23	32.01	2.7960	120.12	280.89	0.6899
24	32.66	2.7419	109.02	149.95	0.4058
25	33.92	2.6430	966.52	797.69	0.2435
26	34.34	2.6112	634.49	523.66	0.2435
27	35.40	2.5357	593.14	489.53	0.2435
28	35.83	2.5065	537.09	591.03	0.3246
29	36.43	2.4660	788.61	650.85	0.2435
30	36.76	2.4450	513.67	423.95	0.2435
31	37.37	2.4066	663.89	639.24	0.2841
32	37.88	2.3755	164.13	135.46	0.2435
33	38.91	2.3147	181.53	224.73	0.3652

34	39.34	2.2906	113.29	124.67	0.3246
35	41.02	2.2003	89.30	61.42	0.2029
36	42.99	2.1041	250.14	172.04	0.2029
37	45.85	1.9792	203.62	224.07	0.3246
38	49.66	1.8358	174.30	263.73	0.4464
39	50.45	1.8088	219.25	211.11	0.2841
40	51.65	1.7697	223.97	215.65	0.2841
41	52.57	1.7411	203.49	167.95	0.2435
42	54.45	1.6851	182.92	176.13	0.2841
43	54.98	1.6702	191.41	210.63	0.3246
44	56.91	1.6181	109.49	120.49	0.3246
45	59.16	1.5618	151.45	229.15	0.4464
46	63.93	1.4563	224.98	247.57	0.3246
47	65.27	1.4296	136.47	112.63	0.2435
48	65.88	1.4179	148.37	265.32	0.5275
49	67.23	1.3925	132.32	291.22	0.6493

Integrated Profile Areas

Based on calculated profile

Profile area	Counts	Amount
Overall diffraction profile	2800592	100.00%
Background radiation	1934085	69.06%
Diffraction peaks	866508	30.94%
Peak area belonging to selected phases	0	0.00%
Unidentified peak area	866508	30.94%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	15121	100.00%
Peak intensity belonging to selected phases	10478	69.30%
Unidentified peak intensity	4643	30.70%

Diffraction Pattern Graphics

Gel 400°c ZnO 2h