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**Treatment of Dye Wastewater Effluents Using  
Synthesized ZnO Nanoparticles: A Box-Behnken Design  
Optimization Approach**

Présenté par :

Prénom et nom : AISSA Bakir

Prénom et nom : ABISMAIL Khaled

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Devant le jury composé de :

|                 |     |            |              |
|-----------------|-----|------------|--------------|
| BENTARFA Djehad | MCB | Université | Président    |
| AOUF Mohamme    | MCB | Université | Encadrant    |
| KHANE Yasmine   | MCB | Université | Co-encadrant |
| FENNICHE Fares  | MCB | Université | Examineur    |
| FEKHAR Bahmed   | MCB | Université | Examineur    |

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# DEDICATION



At the end of this thesis, I would first and foremost like to thank **Allah Almighty**, who granted me the strength and patience to complete this journey.

I also want to acknowledge the efforts I have made and the challenges I have overcome throughout this academic path. I am truly proud of how far I have come.

My deepest gratitude goes to my **beloved parents**, whose unconditional love, constant support, and countless sacrifices made it possible for me to pursue my studies in the best possible conditions. Without them, none of this would have been possible.

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To those who brought love, energy, and encouragement into my life, your support meant more than words can say.

A special thank you to my **friends**, who always believed in me and pushed me to keep going. I wish you all continued success and happiness.

To all of you—and to anyone I may have unintentionally left out—please accept my heartfelt thanks and warmest regards.

*AISSA Bakir*

# DEDICATION



At the end of this thesis, I would like to begin by thanking, first and foremost, **Allah Almighty**, who gave me the strength, patience, and determination to see this work through to the end.

I also want to take a moment to recognize my own efforts—the long hours, the challenges, and the persistence it took to reach this stage. I am proud of how far I have come.

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## Abstract

This study presents an environmentally friendly approach to treating water contaminated with textile dyes, using sustainably synthesized zinc oxide nanoparticles. These nanoparticles were produced through green synthesis using orange leaf extract. Their formation and structural characteristics were confirmed by X-ray diffraction (XRD), UV–visible absorption spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The photocatalytic performance of the nanoparticles was evaluated through the degradation of methylene blue dye under UV irradiation. The effects of pH, temperature, and nanoparticle mass on dye removal were investigated using Response Surface Methodology (RSM), involving 15 experiments to establish a mathematical model. UV-Vis spectrophotometry showed a degradation efficiency of 87.59% for methylene blue after 150 minutes, and nearly complete degradation of Fast Blue R134 after approximately 30 hours. This method offers a sustainable solution to water pollution and paves the way for future research to enhance nanoparticle efficiency and extend their application to other environmental contaminants.

**Keywords:** ZnO NPs, Photodegradation, Methylene Blue, Design of experiments (Box Behnken).

## الملخص

تقدم هذه الدراسة طريقة صديقة للبيئة لمعالجة المياه الملوثة بأصبغ النسيج، والتي تُمثل تحديًا بيئيًا وصحيًا كبيرًا نظرًا للأثار الضارة لهذه المواد على البيئة والصحة العامة. تُسلط الدراسة الضوء على استخدام جسيمات أكسيد الزنك النانوية المُصنَّعة بطريقة مستدامة. تتضمن العملية تخليقًا صديقًا للبيئة للجسيمات أكسيد الزنك النانوية باستخدام مستخلص أوراق البرتقال. وقد تأكد تكوّن جسيمات أكسيد الزنك النانوية من خلال نتائج حيود الأشعة السينية (XRD)، تم تأكيد تكوينها وخصائصها الهيكلية بواسطة حيود الأشعة السينية (XRD) وقياس طيف الامتصاص فوق البنفسجي المرئي وقياس طيف الأشعة تحت الحمراء بتحويل فورييه (FTIR). الشكل الكروي لجسيمات أكسيد الزنك النانوية. تم اختبار التأثير التحفيزي الضوئي لجسيمات أكسيد الزنك النانوية من خلال التحلل الضوئي لصبغة "أزرق الميثيلين" تحت الأشعة فوق البنفسجية. يتناول هذا البحث دراسة تأثير درجة الحموضة ودرجة الحرارة وكتلة الجسيمات النانوية على إزالة الصبغات باستخدام منهجية تجريبية وهي منهجية الاستجابة السطحية والتي تتضمن 15 تجربة بهدف إيجاد تعبير رياضي.

تُبرز نتائج هذه الدراسة تطوّرًا واضحًا في كفاءة عملية التحلل الضوئي بمرور الوقت، وذلك وفقًا لما تم رصده باستخدام مطيافية الأشعة فوق البنفسجية-المرئية، حيث بلغت نسبة التحلل 87.59% لصبغة الميثيلين الأزرق بعد 150 دقيقة من المعالجة، وقراءة 100% لصبغة Fast Blue R134 بعد نحو 30 ساعة. وتمتاز هذه الطريقة بقدرتها على معالجة تلوث المياه بطريقة فعّالة وصديقة للبيئة في آنٍ واحد. كما تفتح نتائج هذه الدراسة آفاقًا واعدة لأبحاث مستقبلية تهدف إلى تعزيز كفاءة الجسيمات النانوية وتوسيع نطاق استخدامها في معالجة أنواع أخرى من الملوثات البيئية.

**الكلمات المفتاحية:** جسيمات نانوية-أكسيد الزنك، التحلل الضوئي، الأزرق الميثيليني، تصميم التجارب (Box Behnken)

## Résumé

Cette étude propose une approche respectueuse de l'environnement pour le traitement des eaux contaminées par des colorants textiles, en utilisant des nanoparticules d'oxyde de zinc synthétisées de manière durable. Ces nanoparticules ont été produites par synthèse verte à partir d'un extrait de feuilles d'oranger. Leur formation a été confirmée par diffraction des rayons X (XRD), spectroscopie d'absorption UV-visible et spectroscopie infrarouge à transformée de Fourier (IRTF). La performance photocatalytique des nanoparticules a été évaluée à travers la dégradation du colorant bleu de méthylène sous irradiation UV. Les effets du pH, de la température et de la masse de nanoparticules sur l'élimination des colorants ont été étudiés à l'aide de la méthodologie de surface de réponse (RSM), selon un plan expérimental de 15 essais visant à établir un modèle mathématique. Le suivi par spectrophotométrie UV-Vis a montré une efficacité de dégradation de 87.59 % pour le bleu de méthylène après 150 minutes, et une dégradation quasi totale du Fast Blue R134 après environ 30 heures. Cette méthode offre une solution écologique à la pollution de l'eau et ouvre la voie à des recherches futures visant à améliorer l'efficacité des nanoparticules et à élargir leur application au traitement d'autres contaminants environnementaux.

**Mots clés :** NPs-ZnO, Photodégradation, bleu de méthylène, méthodologie expérimentale (Box Behnken).

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## Table of abbreviations

| Abbreviation         | Meaning                      |
|----------------------|------------------------------|
| <b>MB</b>            | Methylene blue               |
| <b>NPs-ZnO</b>       | Zinc oxide nanoparticles     |
| <b>Ec</b>            | Conduction band              |
| <b>Ev</b>            | Valence band                 |
| <b>H<sup>+</sup></b> | Holes                        |
| <b>XRD</b>           | X-ray diffraction            |
| <b>SEM</b>           | Scanning electron microscopy |
| <b>RSM</b>           | Response Surface Methodology |
| <b>FTIR</b>          | Fourier Transform Infrared   |

## General introduction

Water is the most abundant natural resource on Earth, covering nearly 71% of the planet's surface. It's super important for life [1], helps ecosystems thrive, and is essential for farming, industry, and our daily lives. Despite its abundance, the amount of freshwater suitable for human use is limited, making the preservation of water quality a global priority. Access to clean water remains a major challenge in many parts of the world. Billions of people experience periods of water scarcity, while Unsuitable sanitation systems and unsafe drinking water are also the cause of many infectious diseases[2]. These issues emphasize the importance of developing effective and sustainable technologies for water purification.

Rapid industrialization and population growth have significantly increased the discharge of contaminated wastewater into the environment. Currently, the world production of synthetic coloring agents exceeds 800,000 tons per year and this usage has become almost infinite in various fields. Therefore, wastewater treatment technologies need to be improved in order to protect aquatic ecosystems and to use treated water for agricultural, industrial and household needs[3].

Nanotechnology involves the development of materials with dimensions between 1 and 100 nm, where they exhibit unique physicochemical properties. Among these materials, ZnO nanoparticles are widely studied due to their stability, low toxicity, low cost, and excellent photocatalytic activity, which makes them the promising catalysts for the degradation of organic pollutants in wastewater[4].

In order to reuse the cleaned water, this technology was utilized to remove methylene blue dye from industrial wastewater, as part of our senior thesis. This was accomplished by employing semiconductor materials, specifically zinc oxide nanoparticles, which were biosynthesized using green synthesis method.

This thesis contains 3 chapters. The first chapter provides a literature review on colorants in general, nanoparticle (NP) types and synthesizing concepts, in addition to an overview of the plant used in the green synthesis of NPs, and general notions about photocatalytic degradation. The second chapter is dedicated to describing the materials, methods, and techniques followed during the experimental work in the laboratory of process engineering at the faculty of science and technology. The experimental work was basically on the zinc oxide nanoparticles synthesis and their application in a photodegradation process to treat wastewater containing Methylene

Blue (organic dye) using a Box-Behnken experimental design, investigating the effect of pH, Temperature, and mass of NPs on the efficiency of the photodegradation.

Chapter 3 deals with presenting the results of the experiment, characterizing the synthesized ZnO-NPs, and discussing the outcomes of the photodegradation results explaining what could be the main factor influencing the process of dye removal from wastewater.

Finally, a general conclusion closes this work by proposing recommendations for future research.

## I. Chapter I: Theoretical Background

Dyes have been used since ancient times and were originally obtained from natural sources such as plants, animals, fungi, roots, leaves, bark, and berries. Archaeologists have found evidence that textile dyeing goes back to the Neolithic period (around 10,200 BC), while records from China show that dyes were produced from plants, insects, and tree bark approximately 5,000 years ago.(Figure 1). [5]

### I.1. Introduction to dyes

A dye is a colored compound containing chromophore groups, which impart color, and auxochrome groups, which enhance its affinity for substrates. Synthetic dyes are extensively used in industries such as textiles, food, cosmetics, and paper, with the textile industry being the largest consumer[6].

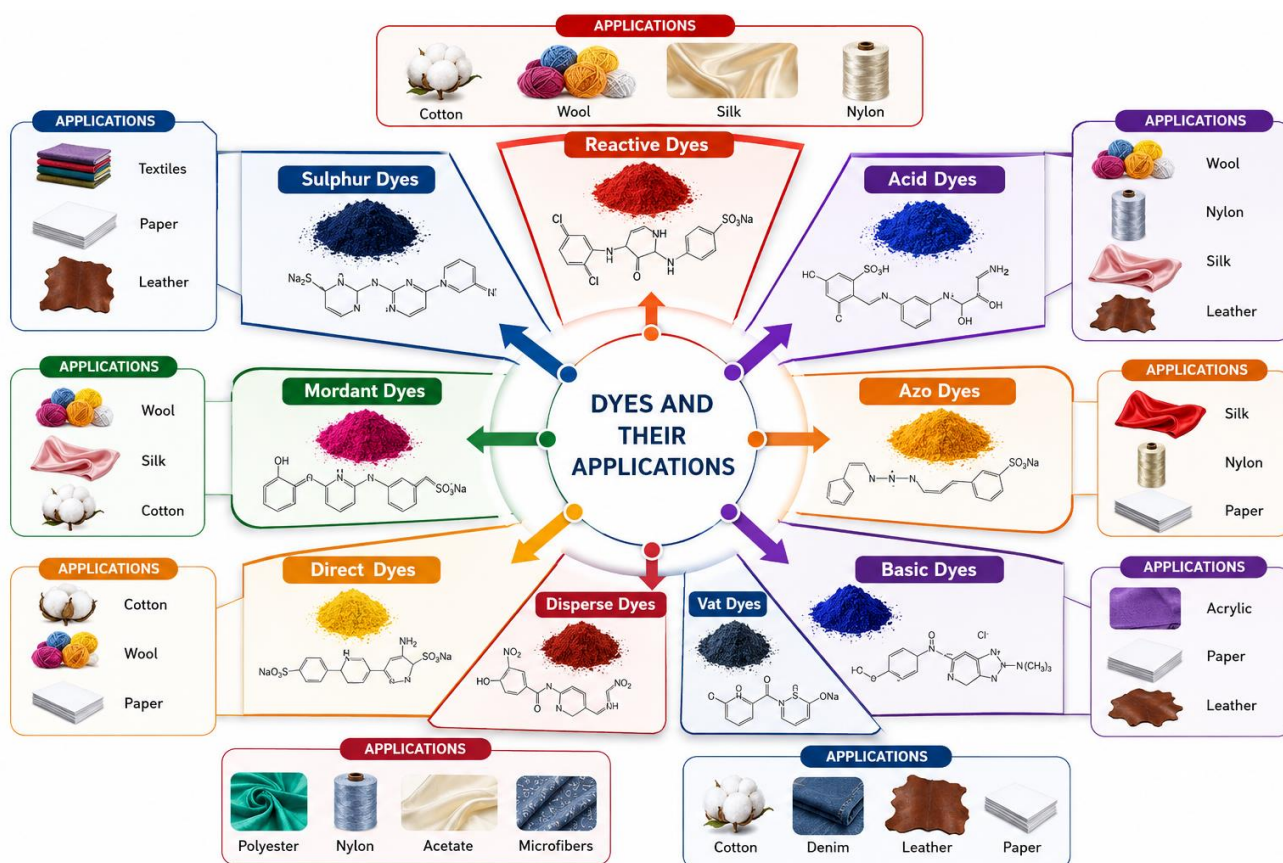


Figure1 : different types of dyes and their applications[5]

### I.1.1 Toxicity of dyes

Textile dyes are considered significant environmental pollutants because they are generally non-biodegradable and can persist in water even at low concentrations. The release of dye-contaminated wastewater may lead to various health problems, including skin **rashes**, **headaches**, nausea, and an increased risk of cancer. Their harmful effects extend to both humans and aquatic ecosystems, with toxicity commonly classified as acute or chronic (genotoxic), the latter being associated with long-term health consequences. Reactive dyes are frequently linked to skin irritation and allergic reactions, whereas ionic dyes can cause skin and respiratory disorders and adversely affect fish and invertebrates. Although common nonionic dyes exhibit relatively low acute toxicity, they may still present carcinogenic risks and negatively influence aquatic plants. Similarly, nonionic aquarium dyes are characterized by low toxicity and have limited effects on aquatic life. Cationic dyes are known to cause skin irritation and respiratory problems, which can harm fish and aquatic plants, while anionic reactive dyes produce similar effects and are also detrimental to aquatic plants. [7]

### I.1.2 The dye studied (Methylene Blue) and its applications

Bis-(dimethylamino)-3,7-phenazathionium chloride or Methylene blue (MB) as it is known, is an azine (thiazine) dye of basic, and cationic family (Figure 2, Figure 3).

MB dye exhibits numerous potential applications in textile, pharmaceutical, paper, dyeing, printing, paint, medical, and food industries. It is the most widely used dye in the textile sector and is regarded as one of the most prominent colors for clothing, it exhibits strong affinity for the interstitial spaces within cotton fibers and demonstrates strong fixation to fabric in textile applications. It is also employed to assess rock swelling, serving as a rapid test for evaluating the quality of aggregates. Furthermore, MB dye is used as a photosensitizer, an oxidation-reduction indicator, an optical redox indicator in analytical chemistry, and in trace analysis of anionic surfactants. [8]



Figure 2 : methylene blue



Figure 3 : chemical structure of methylene blue

Table 1: Physicochemical properties of MB dye [8]

| Property                       | Description                                                                                                                                                                                                            |
|--------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Physical Form                  | Dark green, odorless powder at room temperature, yielding a blue solution when dissolved in water                                                                                                                      |
| Molecular Diffusivity          | $D_{\text{mol}} = 4.7 \times 10^{-6} \text{ cm}^2/\text{s}$ at $25^\circ\text{C}$                                                                                                                                      |
| Molecular Size                 | Length: 13.82–14.47 Å; Width: $\approx 9.5$ Å                                                                                                                                                                          |
| Solubility                     | Soluble in methanol, ethanol, acetone, ethyl acetate, and water (solubility in water: 43.6 g/L at $25^\circ\text{C}$ )                                                                                                 |
| Pka Value                      | 3.8                                                                                                                                                                                                                    |
| Melting Point ( $T_m$ )        | $100\text{--}110^\circ\text{C}$                                                                                                                                                                                        |
| Oxidized and Reduced States    | Blue in the oxidized form, colorless in the reduced form                                                                                                                                                               |
| Chromophore Group              | N–S conjugated system on the central aromatic heterocycle                                                                                                                                                              |
| Auxochrome Group               | Nitrogen-containing groups with lone pair electrons on the benzene ring                                                                                                                                                |
| UV-Visible Absorption Spectrum | <ul style="list-style-type: none"> <li>- Main peak at 664 nm (monomer)</li> <li>- Shoulder peak at 612 nm (dimer)</li> <li>- Additional peaks at 292 and 245 nm (associated with substituted benzene rings)</li> </ul> |

### I.1.3 Toxicity of METHYLENE BLUE dye

Methylene blue (MB) is one of the dyes frequently released by textile industries into natural water bodies, where it poses potential risks to both humans and microorganisms. At high concentrations, MB exhibits considerable toxicity and is recognized as a non-biodegradable and carcinogenic pollutant. Its presence in the environment represents a serious concern because of its adverse effects on both human health and ecosystems. Exposure to MB has been associated with respiratory distress, abdominal disorders, blindness, digestive and mental problems, as well as symptoms such as nausea, diarrhea, vomiting, cyanosis, shock, gastritis,

jaundice, and methemoglobinemia. In addition, it may cause tissue necrosis, increased heart rate, premature cell death in tissues, and irritation of the skin and eyes.

#### I.1.4 Treatment of water contaminated by dyes

The textile industry generates hazardous pollutants such as hydroxylated derivatives, naphthoquinone, phenolic compounds, organic acids, and aromatic amines, leading to persistent environmental challenges. From an engineering perspective, the removal of dyes and pigments from textile effluents is essentially a separation process. Various separation techniques can be applied to eliminate specific components from dye-contaminated wastewater. These treatment methods are categorized into physical, chemical, and biological methods, (Figure 4) [9]. Dye wastewater is treated using various approaches, including those based on physical properties, chemical reactions, and biological activity[10].

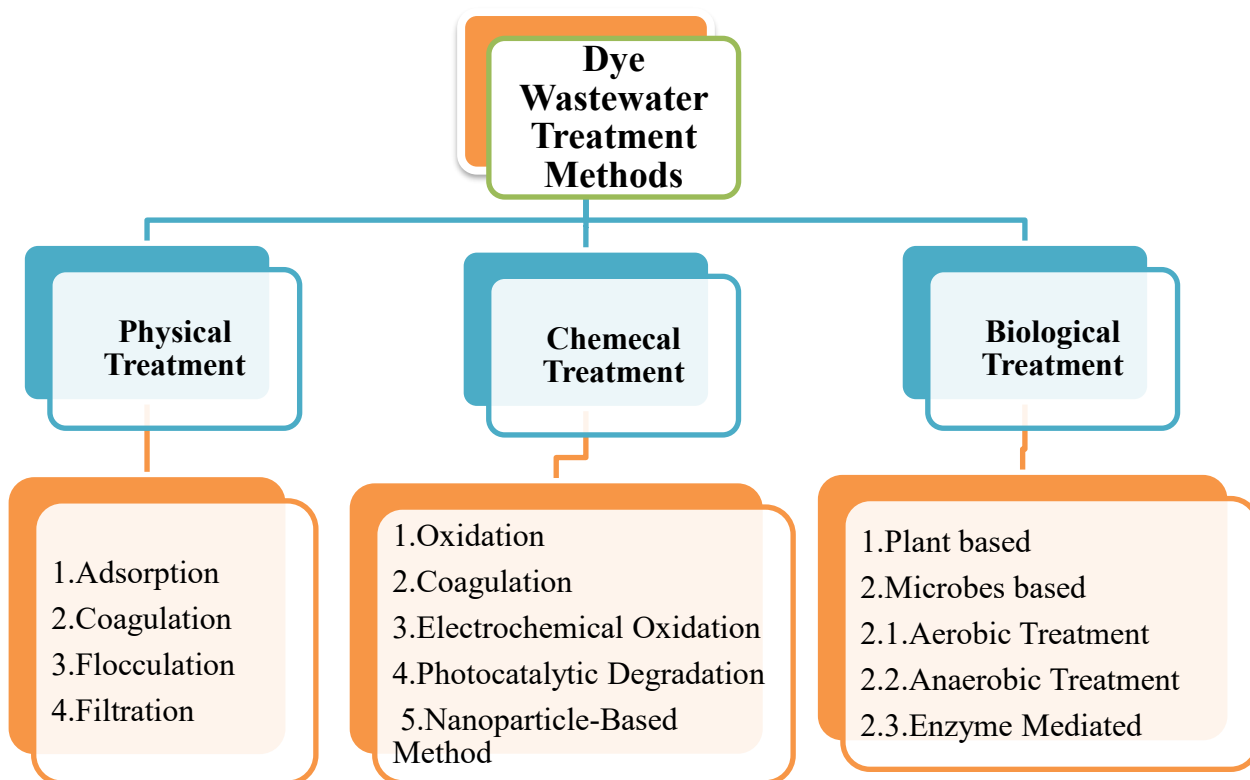


Figure 4: Treatment strategies of dye-containing wastewater.

#### I.2. Generalities on Nanoparticles (NPs)

Nanoparticles (NPs) are ultrafine materials with dimensions measured on the nanometer scale

(1 nm =  $10^{-9}$  m). They occur naturally in the environment and can also be produced through human activities. Their extremely small size gives them distinctive material properties that differ from those of bulk materials. As a result, manufactured nanoparticles have found applications in a wide range of fields, including medicine, engineering, catalysis, and environmental remediation (Figure 5).[11]

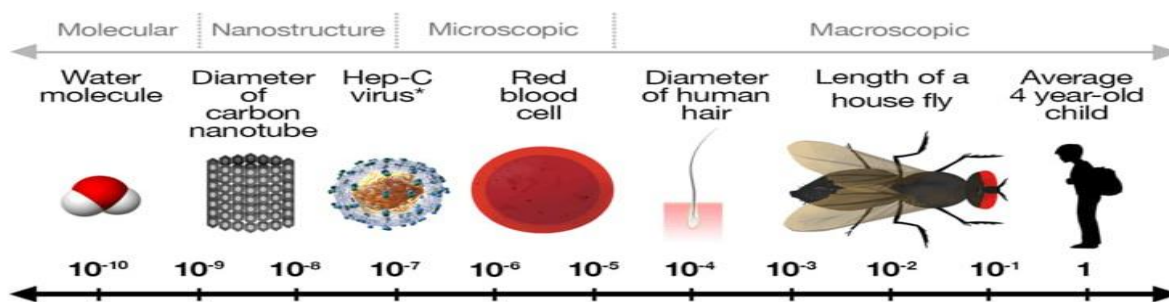


Figure 5: The size scale of nanoparticles

### I.2.1 Classification of NPs

The nanoparticles can be classified according to their source in nature, namely from natural or anthropogenic sources:

### I.2.2 Natural sources

NPs are abundant in nature, as they are produced in many natural processes, including photochemical reactions, forest fires, volcanic eruptions, and simple erosion, and by plants and animals, such as skin and hair shedding, sea spray, clouds, and dust storms.

Natural biological NPs include bacteria, fungi, viruses, proteins (BSA, insulin, etc.), lipids, carbohydrates (glucose, fructose, etc.), and other inorganic biomolecules that are at the nanoparticle level.

Natural NPs are generally monodisperse due to natural selection for size, decreased toxicity, richness in water and hydroxyl groups due to the abundance of hydrated environment, aggregation into complex shapes, and the absence of specific ligands bound to their surfaces.[12]

### **I.2.3 Anthropogenic sources**

#### **I.2.3.1 Accidental NPs (or non-manufactured NPs):**

In this category we find the "ultrafine" atmospheric particles (UFP). These particles are emitted in particular by diesel vehicles, gasoline vehicles and district heating systems.

Apart from UFPS, other NPs are produced by man accidentally, unintentionally or unmanufactured. In this class, there are mainly particles present in welding fumes. NPs are also generated by common indoor activities, such as: cooking, smoking, cleaning and combustion (e.g. Candles, fireplaces). Among the NPs produced also by indoor activities: textile fibers, skin particles, spores, dust mite excreant, chemicals, candle smoke, cooking and cigarettes.[12]

#### **I.2.3.2 Artificial NPs (or manufactured NPs)**

Also known as engineered nanomaterials, these are nanoparticles and nanostructured materials specifically developed for targeted applications, such as nanostructured medical implants. They require comprehensive characterization to minimize unintended adverse effects. The first commercial engineered nanomaterials were produced in the 1940s using aerosol methods, such as fumed silica, followed by the synthesis of silica nanospheres from aqueous solutions in the 1960s. Engineered nanoparticles typically exhibit well-defined geometries—such as spheres, rings, and tubes—including carbon-based nanostructures like fullerenes, carbon nanotubes, and graphene, which possess more uniform structures compared to the irregular forms seen in incidental nanomaterials like carbon soot [13].

NPs can also be classified according to their nature, as organic, carbon-based, and inorganic NPs:

#### **I.2.3.3 Organic NPs**

Organic nanoparticles (ONPs) are synthesized from organic molecules with sizes of 100 nm or less. This category includes ferritin, micelles, dendrimers, and liposomes. Among these, micelles and liposomes possess a hollow interior, commonly referred to as a nanocapsule, and are sensitive to heat and electromagnetic radiation, including light. They are also biodegradable and non-toxic, making them suitable materials for drug delivery applications because of these properties. [14]

#### I.2.3.4 Carbon-Based NPs

Carbon-based nanomaterials have attracted considerable attention because of their potential applications in energy storage and generation, water and wastewater treatment, and biological fields. Carbon exists in several allotropic forms, including diamond, graphite, and buckminsterfullerene. Among these allotropes, graphite is the most thermodynamically stable and, because of its high electrical conductivity, is widely used in electronic applications such as batteries, electrodes, and solar panels. Graphite consists of stacked layers of graphene, whereas graphene itself is composed of a single atomic layer arranged in a two-dimensional honeycomb structure. Owing to its high strength, graphene serves as an important building block for the fabrication of other carbon-based nanoparticles. Based on their structure, carbon nanomaterials are generally classified into two main categories [14].

##### Fullerenes(C60)

Buckminster fullerene (C60) has a cage-like structure made of 60 carbon atoms forming hexagons and pentagons, giving it a soccer ball shape. It is known for resonance stabilization and icosahedral symmetry. C60-based nanostructures like nanotubes, nanorods, and nanosheets are widely used in nanotechnology. Its unique properties allow it to accelerate various reactions and enhance system performance. It can also be chemically modified through different transformations for applications in environmental material synthesis. [14]

- **Graphene and Graphene Oxide (GO)**

Graphene is valued in polymer-based nanoparticles for its excellent mechanical, electrical, and molecular properties, though it faces challenges like complex synthesis and aggregation. Graphene oxide (GO) offers a practical alternative, easily produced via top-down methods. Functional oxygen groups improve GO's surface and dispersion qualities. Its dense SP<sup>2</sup> carbon structure blocks gas molecules, making it effective for use in packaging, electronics protection, and corrosion resistance due to its unique water, thermal, and electrical behavior.[14]

#### I.2.3.5 Inorganic NPs

NPs that lack carbon atoms are known as inorganic NPs. They are typically defined as those composed of metals or metal oxides.

### **I.2.3.6 Metal-Based NPs**

Metal-based nanoparticles are produced at the nanometer scale using either destructive or constructive fabrication methods. Nearly all metals can be synthesized as nanoparticles, with aluminum (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag), and zinc (Zn) being among the most commonly used. Because of their quantum effects and high surface-to-volume ratio, metal nanoparticles exhibit enhanced optical, electrical, catalytic, thermal, and antibacterial properties. Their surface-to-volume ratio depends on the size and shape of the nanoparticles, which directly influences characteristics such as UV-visible sensitivity, electrical conductivity, electronic energy levels, and electron affinity. [14]

### **I.2.3.7 Metal Oxide-Based NPs**

Researchers have shown growing interest in metal oxides during the past few decades due to their enhanced reactivity and efficiency. Positive metallic ions and negative oxygen ions combine to form ionic compounds known as metal oxides. Ionic interactions are strong and stable because of the electrostatic interactions. For instance, NPs of iron (Fe) are readily converted to NPs of iron oxide ( $\text{Fe}_2\text{O}_3$ ) when exposed to oxygen at room temperature, greatly increasing its reactivity in comparison to iron NPs. These oxide-based NPs are synthesized to modify the properties of their metal-based counterparts. Silicon dioxide ( $\text{SiO}_2$ ), titanium oxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) are among the most frequently synthesized oxides. [14]

## **I.2.4 Nanoparticles synthesis methods**

Nanomaterials are manufactured using several methods, which are classified into two main groups: bottom-up method and top-down method.

### **I.2.4.1 Top-down method**

The top-down approach, also referred to as the destructive method, produces nanomaterials by breaking down bulk materials into progressively smaller particles. This reduction process converts larger materials into nanoscale structures through a variety of physical techniques. Common examples of the top-down method include lithography, mechanical grinding or ball milling, laser ablation, spraying, electron explosion, arc discharge, and pyrolysis (Figure 6) [15].

#### I.2.4.2 Bottom-up method

The bottom-up method, also called the structural method, involves building materials from atoms to clusters to nanoparticles. Chemical vapor deposition, liquid gelation, spinning, pyrolysis, and biological synthesis are all examples of bottom-up methods (Figure 6).[15]

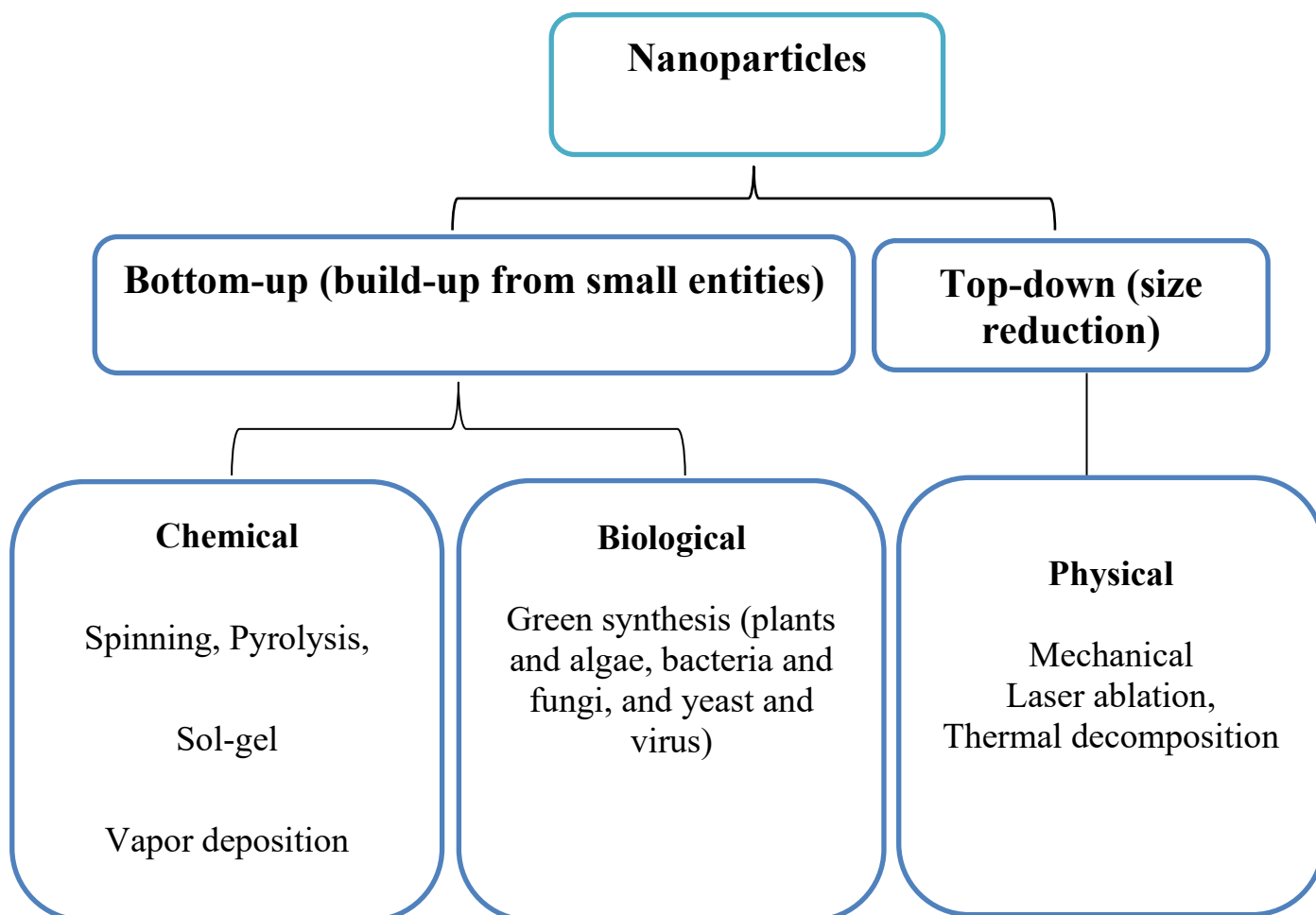


Figure 6: Nanoparticles synthesis methods

#### I.3. Green biosynthesis

Green nanotechnology is an emerging field that combines nanotechnology with sustainable practices to address the environmental and health concerns associated with the conventional synthesis and application of nanomaterials. As awareness of the environmental impacts of traditional manufacturing processes continues to increase, greater attention has been directed toward developing more sustainable and environmentally friendly methods for nanoparticle production and use. This approach focuses on reducing the use of hazardous chemicals,

lowering energy consumption, and promoting the use of renewable resources. Owing to these objectives, green nanotechnology has gained importance for its potential to provide sustainable solutions across a wide range of sectors and to help address major global challenges.[16]

### I.3.1 Synthesis by plants

#### I.3.1.1 Mechanism

In green synthesis, nanoparticles are formed through the reduction of metal ions in the precursor solution by bioactive compounds present in plant extracts. The mechanism of nanoparticle formation may differ depending on the type of plant extract used and the nature of the nanoparticles being synthesized.[16]

Plant extracts contain a wide range of biologically active compounds, such as polyphenols, flavonoids, and terpenoids (Figure 7), which exhibit reducing properties. These compounds act as both reducing and stabilizing agents during nanoparticle synthesis by donating electrons to the metal ions in the precursor solution, thereby promoting their reduction and the subsequent formation of nanoparticles.[16]

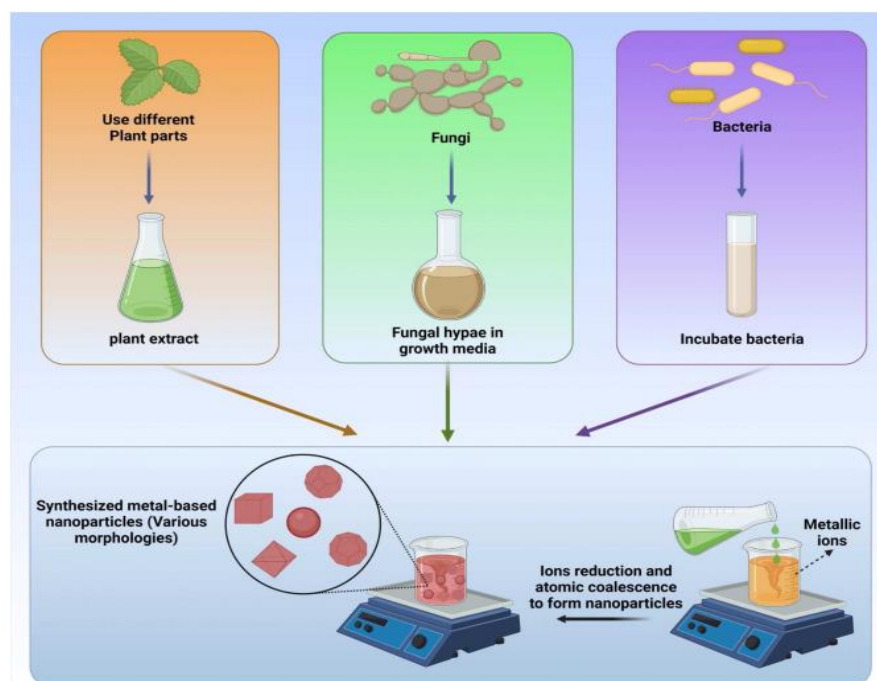


Figure 7: green synthetic routes for NPs[17]

### **I.3.2 Orange leaves**

The orange tree leaves are elliptical or oval leaves that are arranged alternately on the branches of the orange tree, *Citrus sinensis* (Thomson), is an evergreen tree in the Rutaceae family cultivated for its edible fruit.[18]

#### **I.3.2.1 Properties of orange leaves**

The leaves are large, elongated, and pointed, with a smooth, firm surface and a glossy yellowish-green appearance. A characteristic feature of orange leaves is the presence of small heart-shaped wing at the base of each leaf, which distinguishes them from the simple leaves of lemons and limes.[19]

#### **I.3.2.2 The uses of orange leaves**

The main byproducts of orange are peel and leaves. Leaves contain important percentages of proteins and minerals, Citrus fruits and their by-products have received increasing attention because of their contributions to quality attributes through color, antioxidants and flavor.[20]

Orange leaves also could be used to produce essential oil through extraction. Applications of the essential oil extracted from orange leaves in the industry are diverse ranging from food flavoring to cosmetics.[21]

## **I.4. Characterization of NPs**

### **I.4.1 X-ray diffraction (XRD)**

X-ray diffraction (XRD) is a widely used technique for determining the crystal structure and composition of materials. For large crystals, including inorganic compounds and macromolecules, it provides information about the arrangement of atoms within the crystal. When applied to very small crystals, XRD can be used to evaluate the composition, crystallinity, and phase purity of a sample. The technique works by directing X-rays onto the material, where their wavelength is comparable to the spacing between atomic planes. As the X-rays interact with the atoms, they are diffracted at specific angles that depend on the atomic arrangement. While some diffracted beams cancel each other, others undergo constructive interference when they satisfy the required conditions, producing diffraction peaks of higher intensity. The diffraction angle is then related to the spacing between atomic planes through Bragg's law,

$\sin\theta = n\lambda/2d$ , where  $\lambda$  is the monochromatic wavelength of the X-ray source,  $\theta$  is the angle between the incident beam and the diffracting planes, and  $d$  is the interplanar spacing ( $hkl$ ). The calculated interplanar distance can subsequently be used to identify the crystal structure and composition of the material.[22]

#### I.4.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a characterization technique that employs a focused beam of high-energy electrons to produce a variety of signals from the surface of solid specimens. These signals arise from interactions between the electron beam and the sample, providing information about the surface morphology, chemical composition, crystal structure, and crystallographic orientation of the material. The collected data are used to generate two-dimensional images that reveal spatial variations across a selected area of the sample surface. Using conventional SEM, regions ranging from approximately 1 cm to 5  $\mu\text{m}$  can be examined at magnifications from about  $20\times$  to  $30,000\times$ , with a spatial resolution of 50 to 100 nm. In addition to imaging, SEM can analyze selected points on the sample to determine chemical composition qualitatively or semi-quantitatively using techniques such as EDS, EBDS, and EPMA, while EBSD is employed to investigate crystal structure and orientation. The design and operating principle of SEM are closely related to those of EPMA, and the two instruments share many analytical capabilities.[23]

#### I.4.3 Infrared spectroscopy (IR)

Fourier Transform Infrared (FTIR) spectroscopy is an effective technique for identifying the chemical bonds and functional groups present in nanoparticles by measuring their characteristic vibrational transitions in the infrared region. Materials containing infrared-active functional groups can be analyzed directly, allowing the identification of surface chemical species and molecules attached to the nanoparticle surface. FTIR also enables the detection of ligands and other surface modifications in a rapid, accurate, and non-destructive manner. Furthermore, certain nanostructures can enhance the local infrared electromagnetic field, leading to stronger IR signals and improved sensitivity in the characterization and imaging of nanomaterials.

#### I.4.4 UV-Vis Spectroscopy

UV-Visible (UV-Vis) spectroscopy is a simple yet powerful technique used to analyze the absorbance of light by a compound, either in solution or solid form. It works by exciting

electrons from the ground state to an excited state using light in the 200–800 nm wavelength range (1.5–6.2 eV). The principle behind this method is the Beer-Lambert Law: where  $A$  is absorbance,  $\epsilon$  is molar absorptivity,  $b$  is the path length, and  $c$  is the concentration of the sample.

Modern UV-Vis spectrometers generally include a light source (commonly deuterium and tungsten lamps), a sample holder, and a detector. There are three main types of instruments:

- Single-beam, which analyzes one wavelength at a time,
- Double-beam, which compares the sample to a reference for more accurate readings,
- Diode-array (simultaneous), which captures absorbance across the full spectrum instantly and is faster.

Each system has its advantages, but all are effective for studying the optical properties of materials like ZnO nanoparticles.[24]

#### **I.4.5 Zinc oxide nanoparticles NPs ZnO**

Zinc oxide is an inorganic compound of an n-type semiconductor, with the formula ZnO. It is in the form of a white powder and is odorless, insoluble in water, and is widely used as an additive in water.

ZnO is available on the earth's surface in the form of the mineral zincite..[25]

Zinc oxide nanoparticles are used in several fields including the rubber industry because they give the rubber compound abrasion resistance, improve the high polymer performance in its hardness, density, aging resistance, and other functions. Due to the strong UV absorption properties of ZnO, they are widely used, such as cosmetics and sunscreens. Also, zinc oxide nanoparticles have antibacterial, antimicrobial, and anti-ultraviolet properties. Therefore, in the textile industry, the finished fabrics by adding zinc oxide nanoparticles have shown the attractive functions of UV and visible light resistance, antibacterial, and deodorant.[26]

#### **I.4.6 Properties of ZnO nanoparticles**

Zinc oxide nanoparticles (ZnO) are among the most studied due to their potential for diverse application. The physical and chemical behaviors of ZnO-NPs can be easily changed by changing their shape using different synthesis methods, different precursors, or different

materials to produce the nanomaterial. ZnO-NPs have an energy range of 3.37 eV and a binding energy of 60 meV, and they also have low toxicity, high UV absorption, and a solid and rigid structure, which provides excellent chemical, electrical, and thermal stability.[27]

#### I.4.6.1 Crystallographic properties

Zinc is a semiconductor that can crystallize in three distinct structures (Figure: 9): wurtzite, zinc blende, and rock salt. Among these, the hexagonal wurtzite structure is the most thermodynamically stable. This structure features a unit cell with lattice parameters  $a = b = 3.2499 \text{ \AA}$ , separated by an angle of  $120^\circ$ , and a  $c$ -axis of  $5.2060 \text{ \AA}$ , which is perpendicular to the plane formed by  $a$  and  $b$  (as shown in Figure: 8). Each zinc atom is coordinated by four oxygen atoms positioned at the vertices of a tetrahedron. Notably, the zinc atom is slightly displaced by approximately  $0.11 \text{ \AA}$  from the center of the tetrahedron in a direction parallel to the  $c$ -axis. The wurtzite structure maintains its thermodynamic stability at room temperature. In contrast, the cubic zinc blende structure is formed only when grown on cubic substrates, while the rocksalt structure emerges only under relatively high pressures (approximately  $10^{-15} \text{ GPa}$ ).

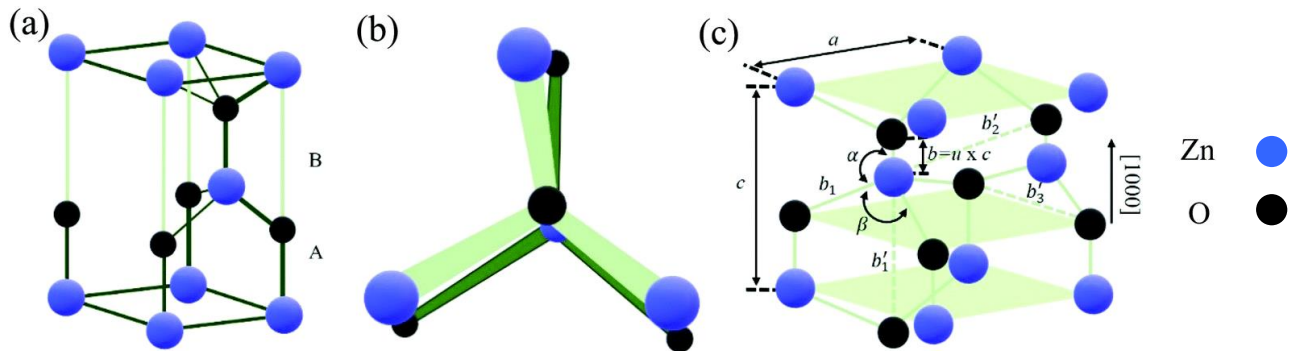


Figure 8: Wurtzite Structure of Zinc oxide[28]

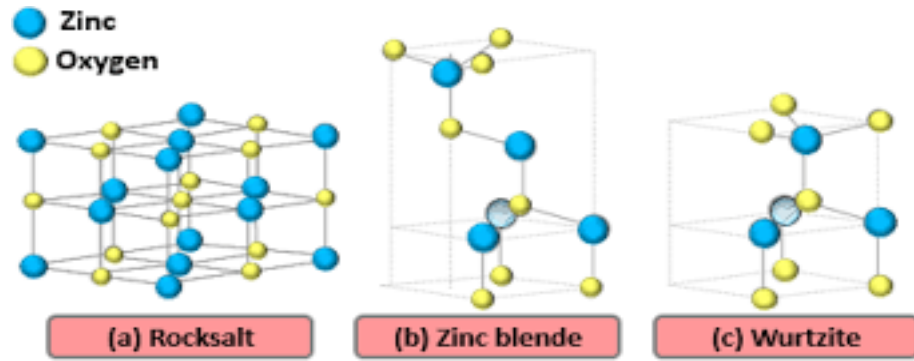


Figure 9: Schematic representation of ZnO structures: a): cubic rocksalt, b): cubic zinc blende, and c): hexagonal wurtzite [28]

Table 2: Main crystallographic characteristics of Zinc oxide NPs

| Crystal Structure                          | Hexagonal Wurtzite                                                                              |
|--------------------------------------------|-------------------------------------------------------------------------------------------------|
| Lattice Parameters                         | $A = 3.2499 \text{ \AA}$ , $c = 5.2060 \text{ \AA}$ , $c/a = 1.6019$                            |
| Bond Length between $O^{2-}$ and $Zn^{2+}$ | Along the c-axis: $d = 1.96 \text{ \AA}$<br>For other nearest neighbors: $d = 1.98 \text{ \AA}$ |
| Ionic Radius                               | $Zn^{2+} = 0.60 \text{ \AA}$ , $O^{2-} = 1.38 \text{ \AA}$                                      |

#### I.4.6.2 Optical properties

The optical behavior of ZnO is largely determined by its wide band gap, which arises from the strong interaction between Zn-3d and O-2p orbitals and the high ionization energy of oxygen. In addition to controlling charge carrier concentration and mobility, doping is widely used to tailor the optical properties of ZnO. For example, alloying ZnO with magnesium (Mg) increases the band gap to values as high as 5.72 eV, whereas cadmium (Cd) incorporation decreases the band gap to approximately 2.51 eV, resulting in a redshift of the absorption edge.[29]

#### I.4.6.3 Thermal properties

The thermal conductivity of wurtzite ZnO (w-ZnO) has been widely investigated using techniques such as scanning thermal microscopy (SThM) and the laser flash method. Measurements performed by Florescu et al. on bulk n-type ZnO crystals grown along the [0001] direction using vapor-phase transport reported room-temperature thermal conductivity values between 98 and 116 W/mK. Later, Özgür et al. applied the same technique to bulk ZnO samples subjected to different thermal treatments and observed a broader range of thermal conductivity

values, from 46 to 147 W/mK at room temperature, indicating that thermal processing can significantly influence heat transport in ZnO.[30]

#### **I.4.6.4 Electrical properties**

The optical and electrical performance of ZnO can be significantly improved through doping with Group III elements, such as aluminum (Al), gallium (Ga), and indium (In). Among these dopants, aluminum is widely used because it enhances the electrical conductivity of ZnO by increasing the concentration of charge carriers. In addition, transition metal (TM)-doped ZnO nanoparticles have attracted considerable interest owing to their improved functional properties and potential applications in electronics, optoelectronics, and photocatalysis.

Manganese (Mn) is considered one of the most suitable transition metal dopants because of its high solubility in the ZnO crystal lattice, allowing efficient incorporation without significantly altering the host structure.[31]

#### **I.4.6.5 Mechanical properties**

Researchers developed a method to measure the mechanical properties of individual ZnO nanobelts using an oscillating electric field inside a Transmission Electron Microscope (TEM). This caused the nanobelts to vibrate, and at resonance, their bending modulus was calculated using elasticity theory. The results showed that ZnO nanobelts are highly sensitive and suitable for use as nanoresonators and nanocantilevers, especially in applications like Atomic Force Microscopy (AFM), due to their flexibility, tunability, and small size.[32]

### **I.5. Application of zinc oxide nanoparticles**

Zinc oxide nanoparticles have attracted significant attention in recent years due to their distinctive optical, electrical, and chemical properties, which have facilitated a wide range of applications. These applications encompass transparent electronics, ultraviolet light-emitting devices, piezoelectric systems, chemical sensors, optoelectronics, and solar cells. Their high photocatalytic activity and environmental compatibility have made them effective in degrading various emerging organic pollutants. Additionally, ZnO has been employed as a raw material in the pharmaceutical and cosmetic industries, as a pigment in paints, concrete, and rubber products, and as a UV filter in textiles, as well as in medical and biological fields.[24]

### **I.5.1 Application in dye-contaminated water treatment**

In terms of industrial pollution, textile industries are a big source of pollution because they use an enormous amount of water and chemicals and release high levels of toxic and non-biodegradable dye waste including Methylene blue. Dyes are extensively used across various textile-related industries due to their beneficial properties, such as bright colors, water resistance, and ease of application. Among all industrial sectors, the textile industry accounts for approximately 60% of total synthetic dye consumption, while the paper and plastics industries contribute about 10% each. The remaining percentage is distributed among other sectors such as leather.[33]

### **I.6. Generalities on heterogeneous photocatalysis**

The term photocatalysis is derived from the Greek words phos, meaning "light," and katalyo, meaning "to decompose" or "break apart." It describes a process in which light energy activates a photocatalyst, thereby promoting or increasing the rate of a chemical reaction.[34]

According to the International Union of Pure and Applied Chemistry (IUPAC), photocatalysis is the field in which light is used as a catalyst. It refers to photocatalytic chemical reactions triggered by the absorption of photons (light energy) by a photocatalyst. Photocatalysts are semiconductor materials that absorb light. The absorbed photons promote an electron from the valence band to the conduction band, which is separated by a forbidden energy gap. This process generates an electron-hole pair within the material. These charge carriers initiate redox reactions with compounds adsorbed on the surface, leading to the formation of radical species, including OH radicals with strong oxidizing power.[35]

There are two types of photocatalysis: homogeneous and heterogeneous.

- Homogeneous photocatalysis is when the reactant and photocatalyst exist in the same phase. Dyes, natural pigments, are the most common examples.
- Heterogeneous photocatalysis, in this type, the reactant and photocatalyst exist in different phases. Transition metal chalcogenides are the most common examples.[34]

### I.6.1 Mechanism of photocatalysis

Photocatalytic reactions begin when a photon with energy equal to or greater than the band gap of a semiconductor is absorbed. This excites an electron from the valence band to the conduction band, leaving behind a hole in the valence band. The excited electron can either reduce a substrate or interact with electron acceptors like  $O_2$ , forming superoxide radical anions ( $O_2^{\cdot-}$ ). Meanwhile, the hole can oxidize organic molecules or react with water ( $H_2O$ ) or hydroxide ions ( $OH^-$ ) to produce hydroxyl radicals ( $\cdot OH$ ) (Figure 10). These radicals are powerful oxidizing agents that can break down organic pollutants like Methylene blue dye. Other reactive species, such as peroxide radicals, also contribute to the degradation process. Photocatalysis is frequently used in environmental cleanup, and it has been extensively reviewed in literature over the past years.[34]

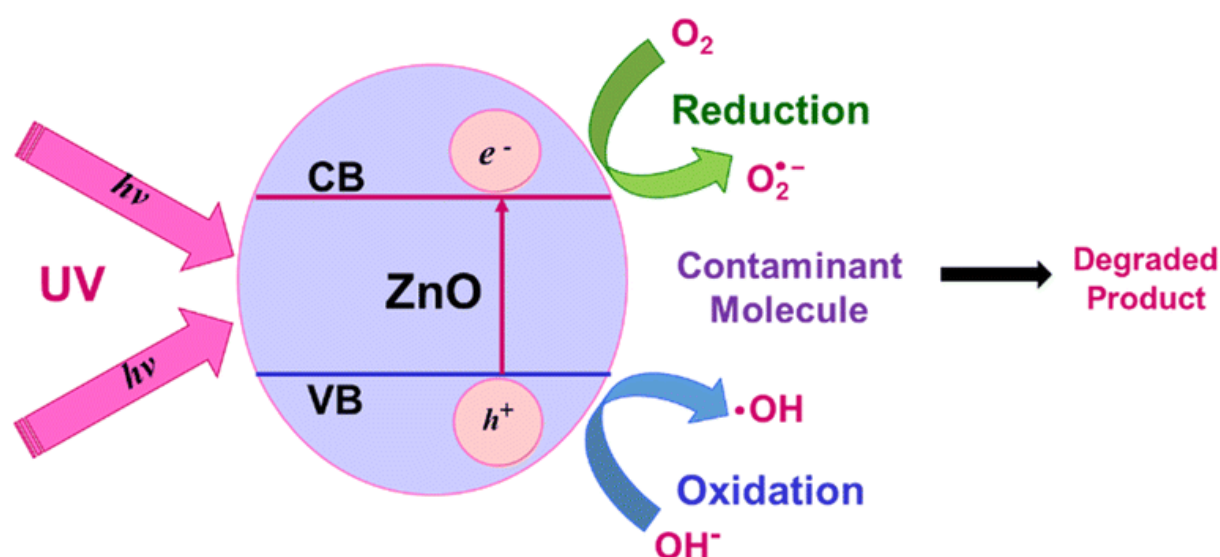


Figure 10: Mechanism of UV-vis photodegradation of ZnO [36]

### I.6.2 Advantages of photocatalysis

- They generate a large number of highly reactive free radicals and far outperform conventional oxidants in terms of decolorization.
- They allow the transformation of refractory pollutants into biodegradable products that can be treated subsequently by less expensive biological treatment methods.
- They ensure complete mineralization of the majority of pollutants into  $CO_2$  and  $H_2O$ .

- They consume less energy than other methods such as incineration.
- They avoid the use of disinfectants and oxidants such as chlorine, the residues of which can have adverse health effects.[37]

### **I.6.3 Disadvantages of photocatalysis**

Advanced oxidation processes (AOPS) in general can produce other unwanted toxic substances as by-products and complete mineralization may not be possible. The presence of radical strippers reduces the efficiency of the processes, some of which are pH dependent.

Prohibitive costs at their current stage of development. [37]

## **I.7. Process optimization methodologies**

Optimization is used to improve system performance and enhance process productivity without increasing operating costs. In conventional practice, the optimum operating conditions are determined by varying one parameter at a time while keeping all other variables constant, an approach commonly known as the one-variable-at-a-time technique. Although this method is straightforward, it does not account for the interactions among variables and, as a result, cannot fully represent their combined influence on the process. To overcome this limitation, optimization studies can be carried out using Response Surface Methodology (RSM), which considers the effects of multiple variables simultaneously.[38]

### **I.7.1 Response Surface Methodology**

Process optimization relies on the application of mathematical and statistical techniques and can be carried out using a variety of approaches. Although several optimization methods have been reported in the literature, Response Surface Methodology (RSM) is widely regarded as one of the most effective techniques. It integrates experimental design, statistical analysis, mathematical modeling, and optimization procedures to determine the optimum operating conditions of a process.[39]

#### **I.7.1.1 RSM application in dye wastewater treatment**

Response Surface Methodology (RSM) is a widely used approach for modeling and optimizing photocatalytic water and wastewater treatment processes. This method helps to evaluate the

linear, interaction, and quadratic effects of various factors on the outcome while providing a predictive model for the response within the range of variables tested. It also identifies the optimal conditions needed to achieve the best performance. Various experimental designs, such as 3k factorial, Doehlert, Box–Behnken, and central composite designs, have been employed to study the treatment of different contaminants, including dyeing effluents, pharmaceutical compounds, and hazardous phenolic substances.[40]

### **I.7.2 Box-Behnken designs**

Box-Behnken designs generally require fewer experimental runs than central composite designs when the same number of factors is considered, making them more economical to perform. They are effective for estimating both first-order and second-order coefficients, although they do not include full factorial experimental runs. In contrast to central composite designs, which employ five levels for each factor, Box-Behnken designs use only three levels per factor. They also avoid experimental combinations in which all factors are set simultaneously at their highest or lowest levels, a feature that distinguishes them from central composite designs[41].

The Box-Behnken design is recognized as a three-level experimental design because it does not include points located at the corners of the experimental region. This characteristic offers a practical advantage when combinations at the extreme levels are either too costly or physically impossible to investigate. By incorporating points at the intermediate levels, the design enables efficient estimation of the coefficients required for a second-order model.[42]

#### **I.7.2.1 Applications of Box-Behnken designs**

Box–Behnken Design (BBD) has been widely applied in various scientific fields due to its efficiency in modeling and optimizing processes. In pharmaceutical product development, BBD is utilized to optimize formulation variables and analytical conditions, ensuring improved drug efficacy and stability [42]. It is also employed in the optimization of spectroanalytical methods, enhancing sensitivity and analytical performance through systematic experimental design [43]. Additionally, BBD plays a crucial role in environmental science, particularly in optimizing conditions for the removal of contaminants using magnetic nanocomposites, thereby improving pollutant remediation efficiency. [43]

## II. CHAPTER II: MATERIALS AND METHODS

This chapter will present all the materials, equipment and experimental methods that were used in this research. It will also provide a description of the different steps of zinc nanoparticles synthesis, as well as the photocatalysis process, and the design of the Box-Behnken experimental plan. This experimental section was conducted in the educational laboratory of the Faculty of Science and Technology of the University of Ghardaïa.

### II.1. The work steps

Figure 11 represents the essential steps followed during the experimental part; each step will be elaborated in the next sections.

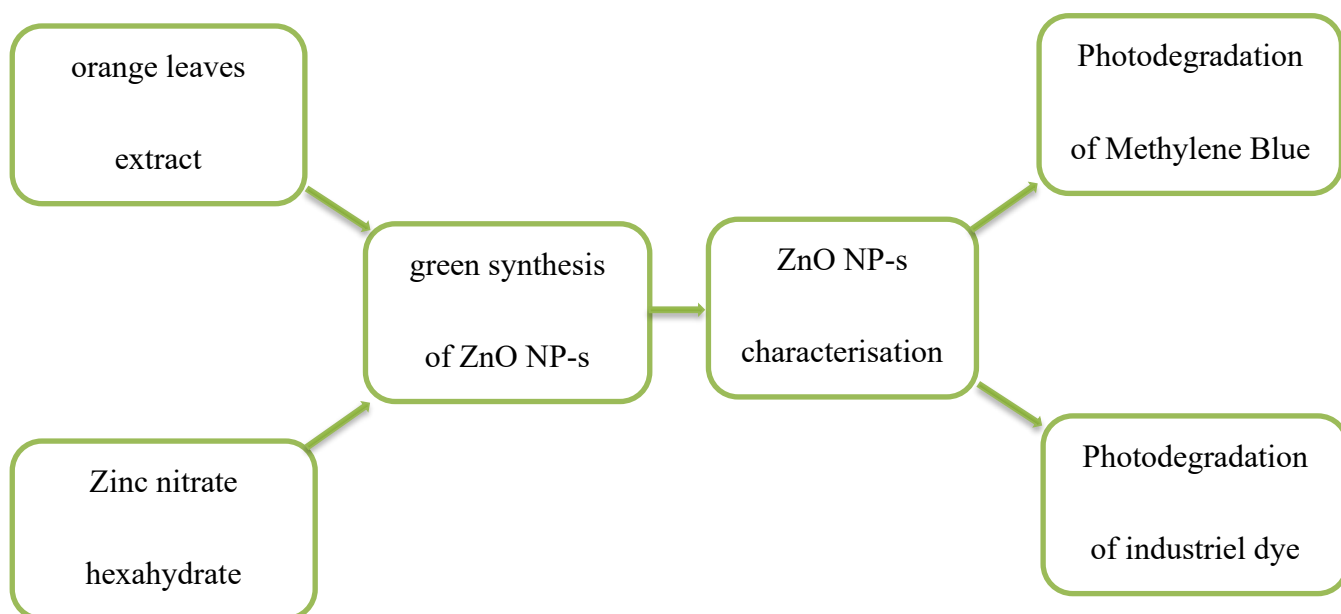


Figure 11: Descriptive chart of the work methodology

#### II.1.1 Materials

The following table lists the essential chemical materials used in our study.

Table 3 : Chemical products used

| Chemical Products        | Chemical name                                        | Molar Mass<br>(g/mol) | Supplier            |
|--------------------------|------------------------------------------------------|-----------------------|---------------------|
| Ethanol                  | C <sub>2</sub> H <sub>6</sub> O                      | 46.08                 | Honeyzell           |
| Zinc nitrate hexahydrate | Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 219.49                | PROLABO "CHEMICALS" |
| Sodium Hydroxide         | Naoh                                                 | 40                    | PROLABO "CHEMICALS" |
| Hydrochloric acide       | Hcl                                                  | 36.5                  | PROLABO "CHEMICALS" |
| Sodium Chloride          | Nacl                                                 | 58.88                 | PROLABO "CHEMICALS" |
| Methelyne blue (MB)      | C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub> S   | 319,85                |                     |

#### II.1.1.1 Origin of the used orange leaves

Orange leaves were chosen as a source for the green reduction process due to their availability. In this study, naturally abscised orange leaves were manually collected from the ground of a garden in Ghardaïa city (south of Algeria), specifically in tmaskht Bounoura, as shown in figure 12.



Figure 12: Geographic distribution of orange leaves

### II.1.2 Preparation of orange leaf extract

The collected leaves were washed to remove impurities and dust then dried in an oven at 60°C for 20 hours. After that, the dried orange leaves were ground to obtain a powder which is then used in the extraction process. For the extraction process, 1 g of orange leaves powder was placed in a beaker containing 100 ml of distilled water. After mixing everything well, the mixture was heated to 60°C while stirring with a magnetic stirrer for 30 minutes. The extract was then filtered using a vacuum filter, stored in a clean, tightly sealed bottle, in the refrigerator for future use. Figure 13 shows the different extraction steps.[43]

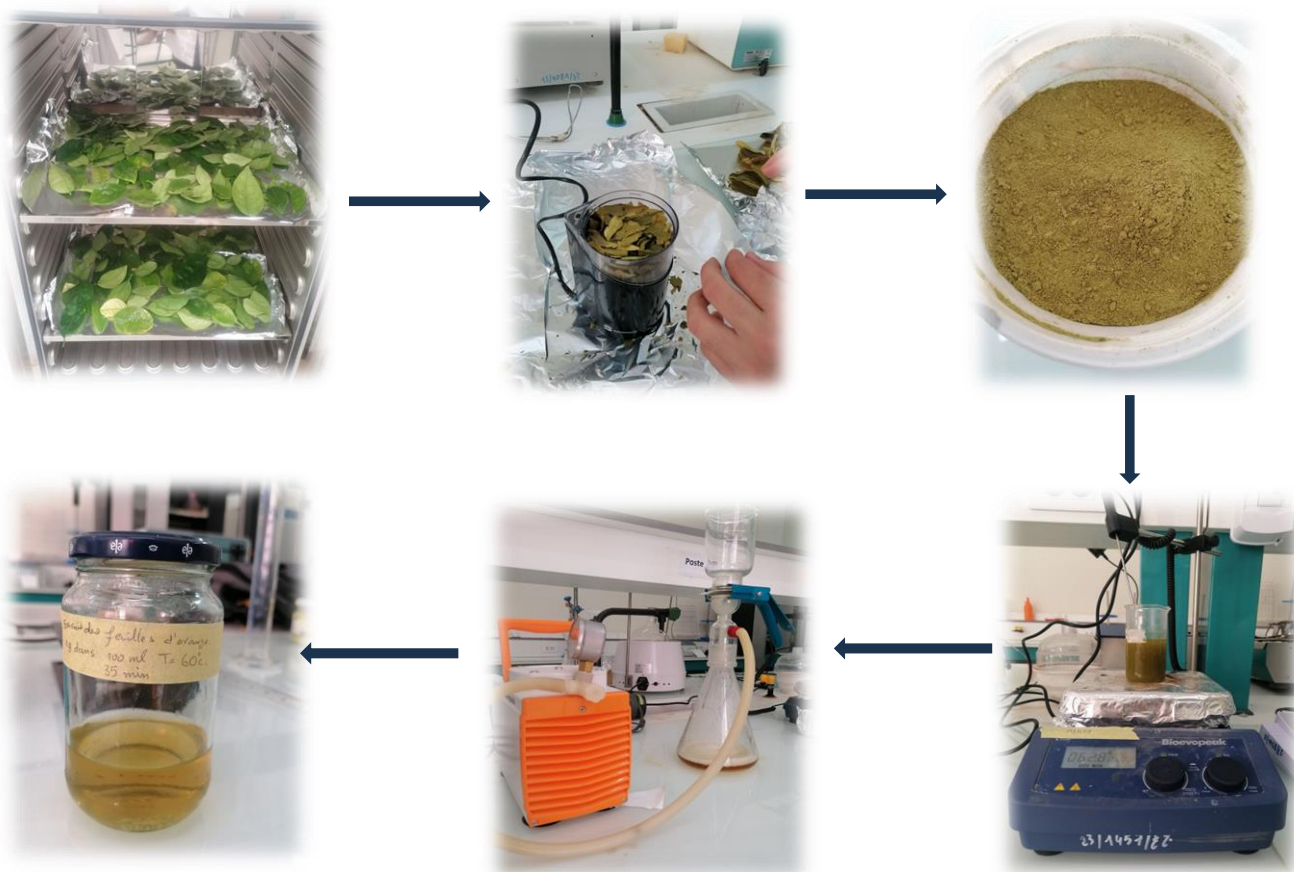


Figure 13: The steps of preparing orange leaf extract

### II.1.3 Green synthesis of nanoparticles

To synthesize zinc oxide (ZnO) nanoparticles, an environmentally friendly green chemistry approach was employed. The synthesis method was adapted from the procedure described by Muthuvel et al.[43], with several modifications.

Initially, 9.97 g of zinc nitrate dihydrate was dissolved in 500 ml of distilled water at room temperature. Separately, a 2 M sodium hydroxide (NaOH) solution was prepared to adjust and stabilize the pH at 12. Subsequently, 20 ml of orange leaf extract was added dropwise to the zinc nitrate solution under continuous stirring at 60 °C. Following the complete addition of the extract, the NaOH solution was gradually introduced dropwise until the desired pH was maintained. The resulting mixture was maintained under continuous stirring at 60 °C for two hours, during which the formation of white ZnO nanoparticles was observed. After that the solution was allowed to settle and water was removed, and the remaining content was subjected to centrifugation. The formed ZnO was rinsed once with distilled water and twice with ethanol to purify the product. Finally, the formed ZnO was carbonized at 400 °C for two hours to complete the nanoparticle synthesizing process.

The synthesis protocol for ZnO-NPs is summarized through the procedural images in figure 14.

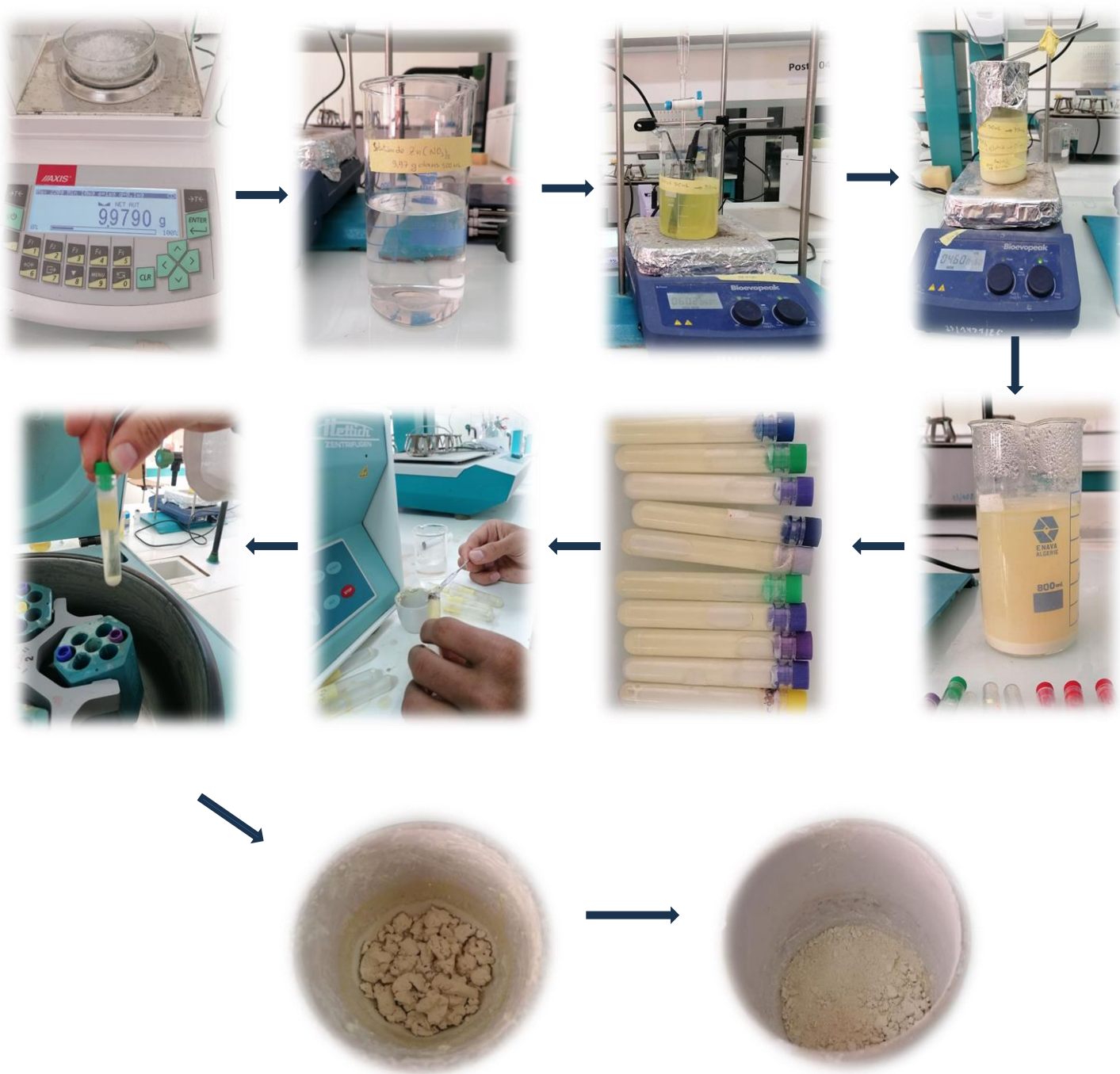


Figure14 : The synthesis protocol for ZnO-NPs

## II.2. Characterization

UV-Vis spectroscopy was used to analyze the optical properties of ZnO samples, and to determine the band gap the Tauc plot method was used. The Tauc relation is expressed by the equation: And the band gap energy ( $E_g$ ) was obtained by plotting  $(\alpha h \nu)^2$  versus  $(h \nu)$  and extrapolating the linear region to the x-axis.

XRD was used to determine the crystal structure of ZnO nanoparticles, SEM to examine their morphology, size, and shape, and FTIR to identify functional groups and assess their chemical structure and surface characteristics.

### **II.2.1 Point of zero charge (PZC) of ZnO NPs**

Using the pH drift approach and applying a 0.1 M NaCl solution as electrolyte, the point of zero charge (PZC) specific to the ZnO nanoparticles was calculated. The pH was set at 2, 4, 6, 8, 10, and 12 for the NaCl solution, and adjusted using 0.1 N NaOH and HCl. A fixed quantity of 0.1 g of ZnO nanoparticles was added to each pH buffer containing 50 ml solution. Control experiments containing ZnO nanoparticles were performed in parallel with six additional flasks at pH 2, 4, 6, 8, 10, and 12 to evaluate the changes in pH. All flasks were placed on a shaker for 20 hours at 150 rpm for the suspension to achieve pH equilibrium. Samples were filtered, and pH measurements were done after 24 h. Data depicting the dependency of the ending pH on the starting pH were constructed.

### **II.3. Application to photodegradation**

To evaluate the effectiveness of the synthesized nanoparticles in the photodegradation of dye contaminants from wastewater, a series of tests was conducted using methylene blue (MB) dye, which is commonly employed in the textile industry.

### **II.4. Preparation of the MB Dye Solution**

When methylene blue (MB) was analyzed with a UV-Vis spectrophotometer, a distinct absorbance peak at its unique wavelength of 664 nm was seen, indicating that the detection was successful.

The absorbance of a number of standard MB solutions with various known concentrations of 0, 1, 2, 4, 6, 10, 20, and 30 ppm were measured in order to create a calibration curve. Plotting the absorbance values against concentration revealed a linear relationship that was in line with the Beer-Lambert Law.

6.6 ppm was chosen as the concentration for all ensuing tests.

To plot the concentration-time curve and obtain the time that yields the best absorbance, we prepared 2 mg of MB dye with a concentration of 6.6 ppm, and measured the absorbance using a uviline®SERIE spectrophotometer by SECOMAM.

#### II.4.1 Photodegradation Protocol for Methyl Blue

In the photodegradation study, we examined the effect of PH, Temperature, and ZnO NPs mass used on the photodegradation, but before that we studied the degradation kinetics over time to set the duration for all the upcoming experiments.

The following procedure was carried out for all the subsequent photodegradation experiments (figure 15):

A 20 ml of methylene blue (MB) dye solution was used either as control (without ZnO nanoparticles) or with presence of ZnO NPs (0.1 g). Both the samples were kept in dark for 30 minutes to achieve an adsorption equilibrium. They were then exposed to UV light of 18 W lamp, and the absorbance was measured at 664 nm using UV-Vis spectroscopy. Before each measurement, the samples were centrifuged at 4000 rpm for 5 minutes. The concentration was determined through a calibration curve. And removal rate was calculated by applying this formula:  $R(\%) = ((C_0 - C) / C_0) \times 100$ , where  $C_0$  is the initial concentration

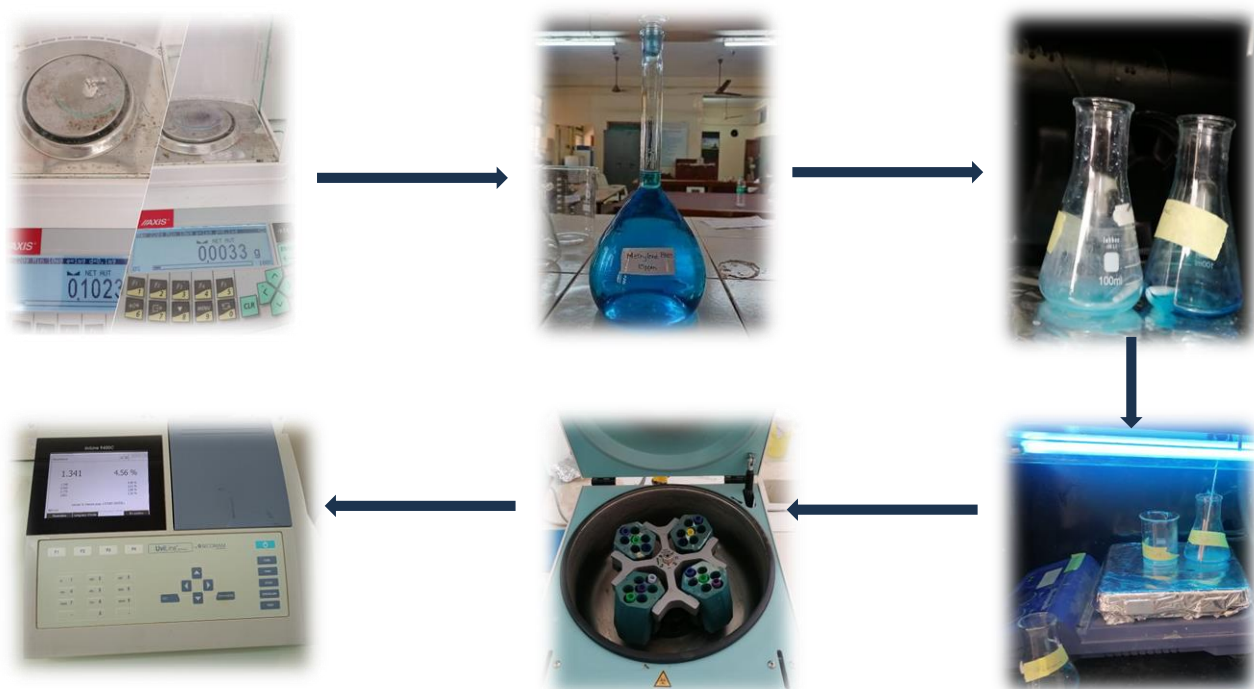


**Figure 15: Photodegradation Protocol for Methyl Blue**

### The application on the industrial dye-contaminated wastewater

A sample of industrial wastewater contaminated with dye (Fast bleu R 134, 0.8%) was collected to test the optimum operating conditions on, which are : (Temperature = 40°C , pH=11, ZnO mass= 0.1g). The absorbance was measured each 10 minutes for the first hour and each 30 minutes for the second, to inspect the degradation of dye. (figure 16)

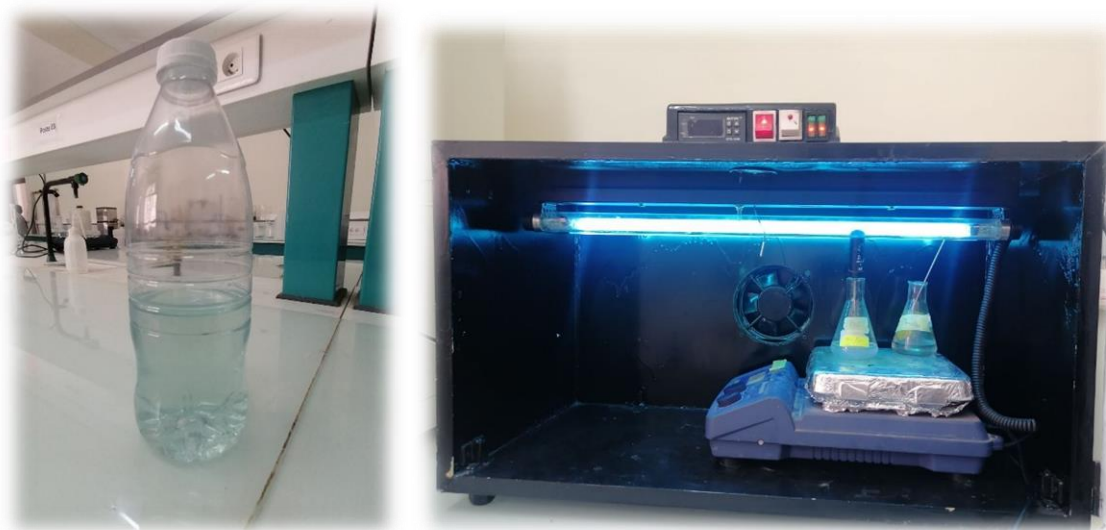


**Figure 16: Photodegradation application on Fast bleu R134, 0.8%**

### II.5. Statistical analyses

The experimental data from the Box-Behnken design (BBD) were evaluated using Statgraphics. The following analyses were employed to evaluate the significance of the model and each factor:

The analysis of variance ANOVA, is considered statistically significant When the P-value is less than 0.05, Moreover, response surface and interaction plots were created to show the interaction effects between variables, where the main effect plots were used to identify the most significant elements influencing the answer. These tools made it simpler to understand how each parameter affected the outcome and to optimize the conditions of the process.

### **Design of experiments**

An experimental design of 15 duplicated tests were conducted once the equilibrium time was identified. The absorbance was measured each 30 minutes for 2 hours, which were carried out according to our standardized procedure of photodegradation. In this design, the factors of temperature, ZnO mass, and pH were systematically varied to assess their effects on the photodegradation process over time.

### III. CHAPTER III: Results and Discussion

This chapter will present the results of the synthesized NPs and their characterization in addition to the discussion of their application on photodegradation

#### III.1.1 PH of point zero charge ( $\text{ph}_{\text{pzc}}$ )

The characterization of The  $\text{ph}_{\text{pzc}}$  of ZnO NPs by determining the pH at zero charge is presented in Figure 17. It confirms the basic nature of surface of the ZnO NPs, which is ( $\text{ph}_{\text{pzc}} = 8$ ), many other researchers have found that the surface of synthesised ZnO NPs has a basic character, Alireza KHATAEE et al 2016, Also Yashni Gopalakrishnan et al 2021

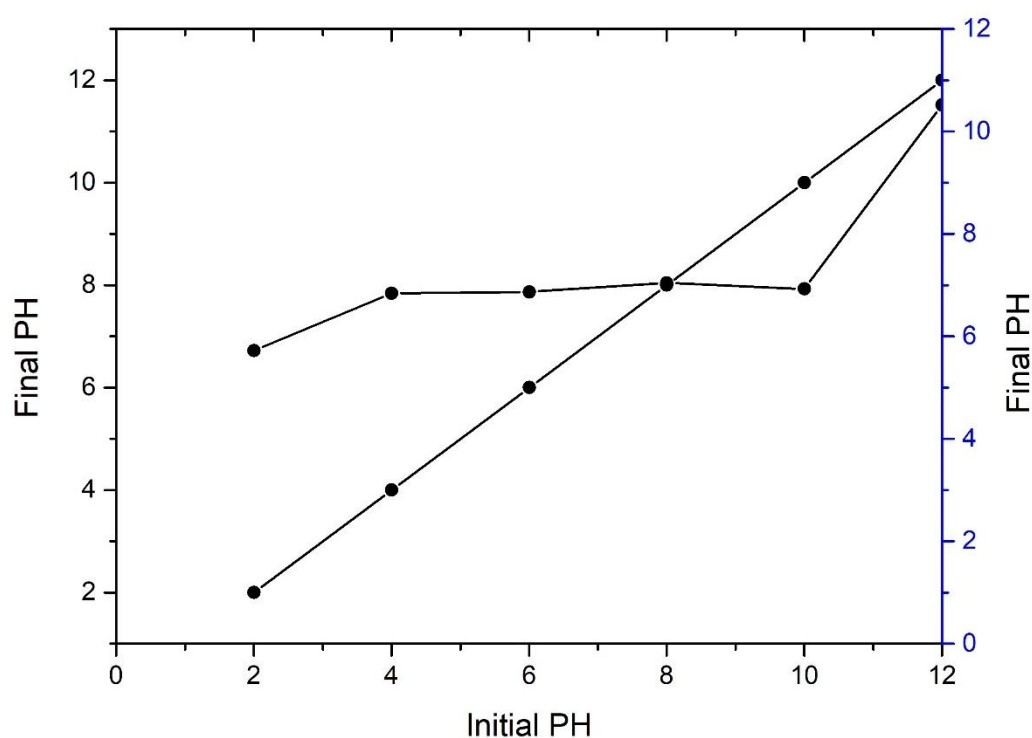


Figure 17: point zero charge ( $\text{ph}_{\text{pzc}}$ ) of ZnO

#### III.1.2 Calibration curve

A calibration curve of absorbance “A” versus concentration “C” (mg/L) of methylene blue (MB) was obtained using different (MB) solutions with concentrations ranging from 0 to 30 mg/L.

The coefficient of determination  $R^2$  is close to unity ( $R^2=0.9819$ ), indicating a good linear correlation between absorbance  $A$  and concentration  $C$  of (MB), as shown in figure 18.

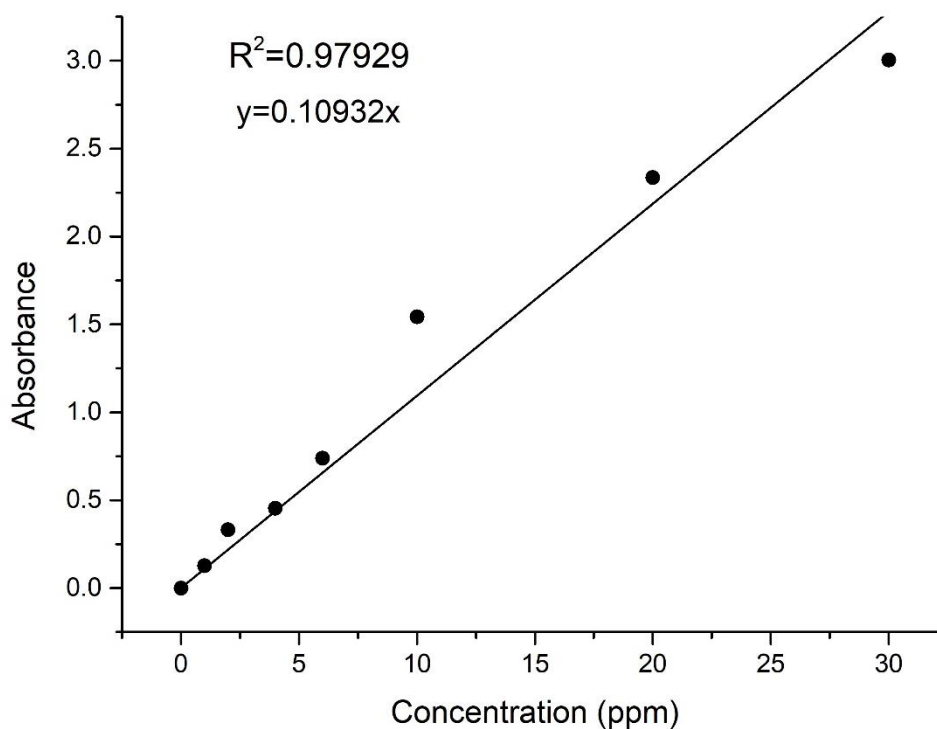


Figure 18 :calibration curve of methylene blue

### III.2. Characterization of Zinc Oxide NPs

The UV-Vis absorption spectrum of ZnO nanoparticles is shown in Figure 19. It has an absorption peak at 369 nm. This confirms that ZnO nanoparticles are formed.

The absorbance is high in the UV region, After the maximum absorption peak at 369 nm, the absorbance decreased progressively with increasing wavelength. Similar absorption behavior for synthesized ZnO nanoparticles has been reported by D K.SINGH et al.[44]

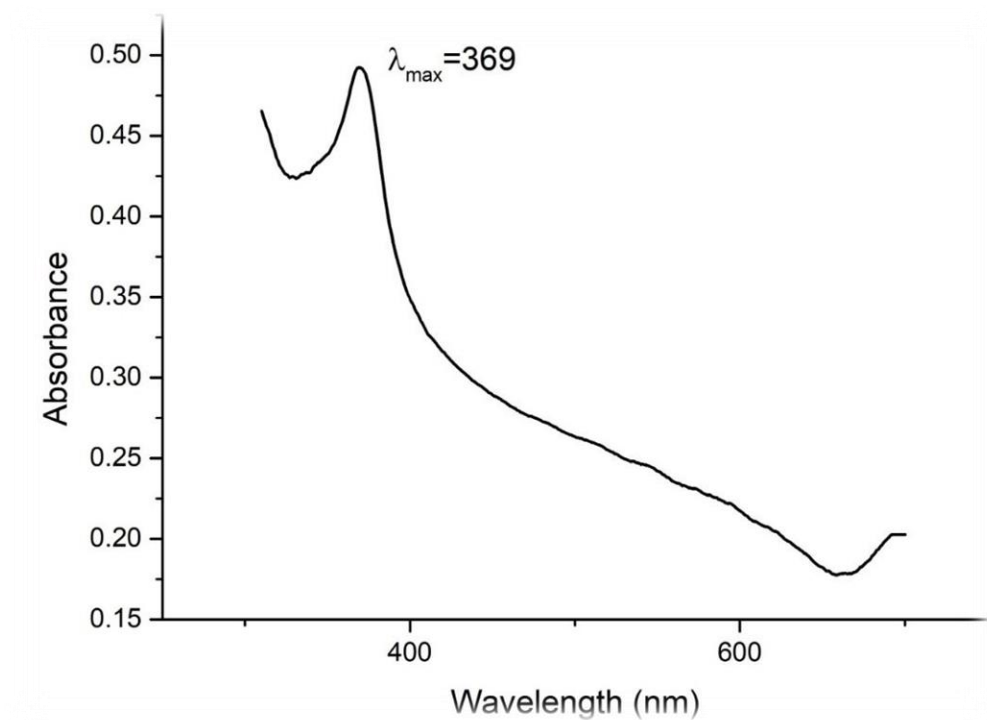


Figure 19: the absorbance curve of ZnO

### III.2.1 Tauc plot

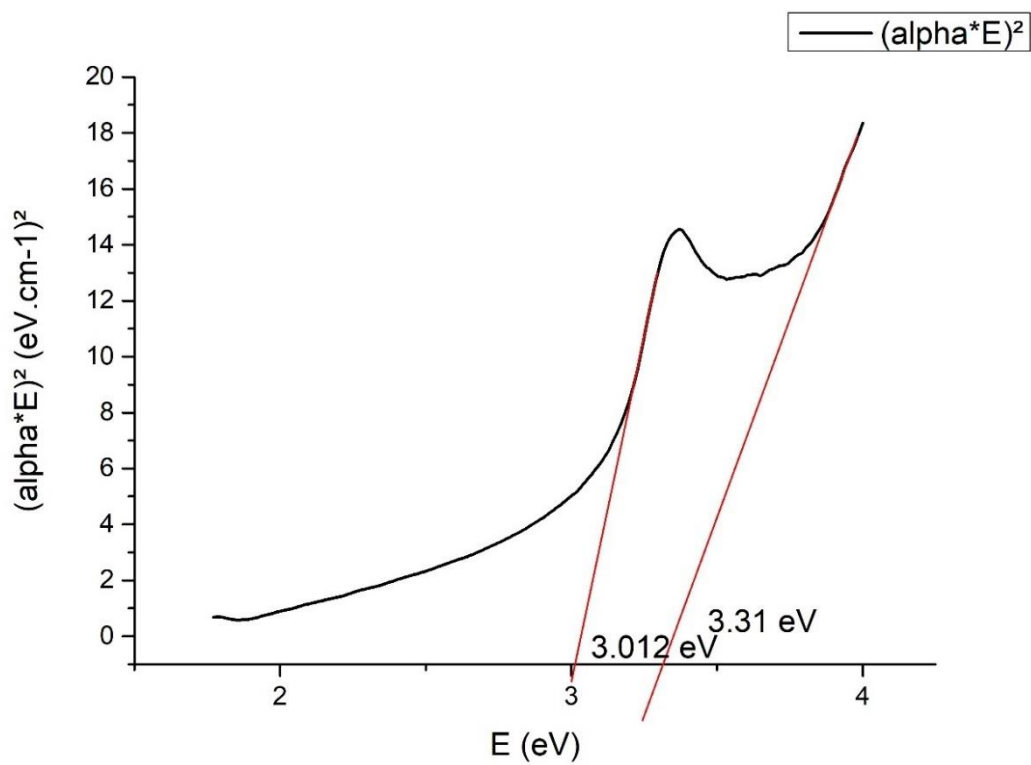


Figure 20: Tauc plot of ZnO NPs

The optical band gap of the synthesized ZnO nanoparticles was determined using Tauc plot analysis derived from UV–Vis absorption data (Figure 20). The plot of  $\alpha h\nu$  versus photon energy, applicable for direct band gap semiconductors like ZnO, exhibited two distinct linear regions. Extrapolating these lines to the energy axis yielded band gap values of 3.012 eV and 3.31 eV. The lower value of 3.012 eV is noticeably below the typical band gap range for ZnO, which generally lies between 3.2 and 3.4 eV, depending on factors such as particle size, crystallinity, and synthesis method [45][46]. In an ideal scenario—where ZnO nanoparticles are highly crystalline, stoichiometric, and defect-free—a single absorption edge around 3.3 eV would be expected [47]. The appearance of the lower energy transition is possibly originating from oxygen vacancies, zinc interstitials, or surface states frequently seen in nanostructured or green-synthesized ZnO, the appearance of the lower energy transition most likely reflects defect-related or localized electronic states within the band gap. In the meantime, ZnO's intrinsic optical band gap is confirmed by the transition at 3.31 eV, indicating that it is semiconducting. The coexistence of both transitions implies that both extrinsic defect states and intrinsic band structure contribute to the optical behavior.

### III.2.2 FTIR analyses

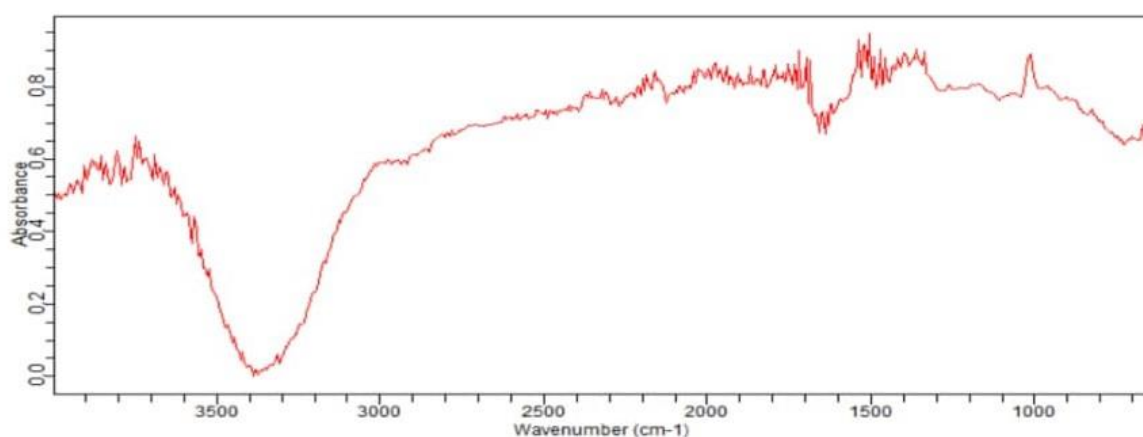


**Figure 21: FTIR spectrum of green-synthesized ZnO NPs**

The FTIR spectrum of green-synthesized ZnO nanoparticles (Figure 21), recorded in the range of 3500–1000  $\text{cm}^{-1}$ , provides valuable information regarding their surface chemistry. A broad absorption band observed near 3400  $\text{cm}^{-1}$  is attributed to O–H stretching vibrations, which indicates the presence of surface hydroxyl groups or adsorbed water—features commonly associated with ZnO nanoparticles synthesized via green or aqueous routes [48]. In the region of 1030–1085  $\text{cm}^{-1}$ , weaker absorption bands suggest the presence of C–O stretching vibrations, likely arising from residual organic compounds or phytochemical capping agents originating

from the plant extract used during synthesis [44]. While the characteristic Zn–O stretching vibrations typically appear below  $1000\text{ cm}^{-1}$ , they have been well-documented in the  $381\text{--}403\text{ cm}^{-1}$  and  $480\text{--}634\text{ cm}^{-1}$  ranges, further confirming the successful formation of ZnO nanoparticles. Altogether, the FTIR data confirm both the structural integrity of the ZnO nanoparticles and the presence of surface functional groups, consistent with findings reported in previous studies on biologically and chemically synthesized ZnO nanomaterials [45].

### III.2.3 X-Ray Diffraction Analysis of ZnO Nanoparticles

The XRD analysis was performed using an EMPYREAN diffractometer under the following operating conditions (Figure 22):

**Table 4: operating conditions**

| Parameter               | Value                                        |
|-------------------------|----------------------------------------------|
| Radiation source        | Cu K $\alpha$                                |
| Wavelength              | $1.5406\text{ \AA}$                          |
| Voltage                 | 40 kv                                        |
| Current                 | 30 ma                                        |
| Scan range              | $5^{\circ}\text{--}90^{\circ}$ ( $2\theta$ ) |
| Step size               | $0.026^{\circ}$                              |
| Measurement temperature | $25^{\circ}\text{C}$                         |
| Scan mode               | Continuous                                   |

The X-ray diffraction pattern of the prepared zinc oxide nanoparticles (figure shows some distinct and sharp peaks, indicating that there is high crystallinity in the compound. The diffraction peaks are consistent with those expected for the wurtzite hexagonal crystal structure of ZnO.

According to V.P.Dinesha et al 2014, The diffraction peaks of ZnO nanoparticles were determined using the crystal structure of hexagonal wurtzite ZnO together with Bragg's law. First, a crystallographic plane such as (100) is selected. Then, the interplanar spacing "d" between the crystal planes is calculated using the hexagonal lattice equation:

Where  $a$  and  $c$  are the lattice parameters of ZnO. After calculating the d-spacing, Bragg's law is applied:

Using the Cu K $\alpha$  wavelength ( $\lambda=1.5406$ ), the diffraction angle  $2\theta$  is obtained. This method gives the characteristic ZnO peaks near  $31.7^\circ$ ,  $34.4^\circ$ ,  $36.2^\circ$ ,  $47.5^\circ$ , and  $56.6^\circ$ , corresponding respectively to the (100), (002), (101), (102), and (110) crystallographic planes.[49]

**Table 5: comparison between our samples and the standard ZnO (JCPDS 36-1451)**

| Standard ZnO (JCPDS 36-1451) | Our Sample    | Plane (hkl) |
|------------------------------|---------------|-------------|
| $31.7^\circ$                 | $31.95^\circ$ | (100)       |
| $34.4^\circ$                 | $34.55^\circ$ | (002)       |
| $36.2^\circ$                 | $36.40^\circ$ | (101)       |
| $47.5^\circ$                 | $47.60^\circ$ | (102)       |
| $56.6^\circ$                 | $56.70^\circ$ | (110)       |

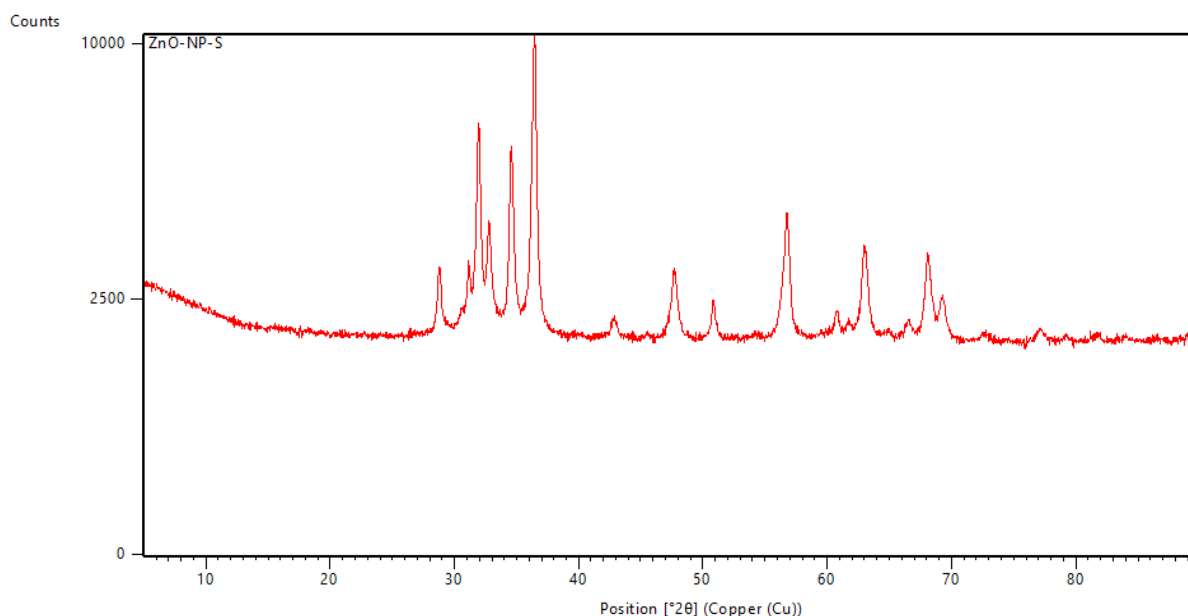


**Figure 22: X-ray diffraction (XRD) pattern of ZnO NPs**

### III.2.4 SEM analysis of ZnO Nanoparticles

SEM images at different magnifications (1  $\mu\text{m}$ , 500 nm, and 200 nm) revealed quasi-spherical ZnO nanoparticles in the nanometer range. EDS analysis showed that zinc and oxygen were the predominant elements, accounting for approximately 60% and 25%, respectively, confirming the successful synthesis of high-purity ZnO nanoparticles.

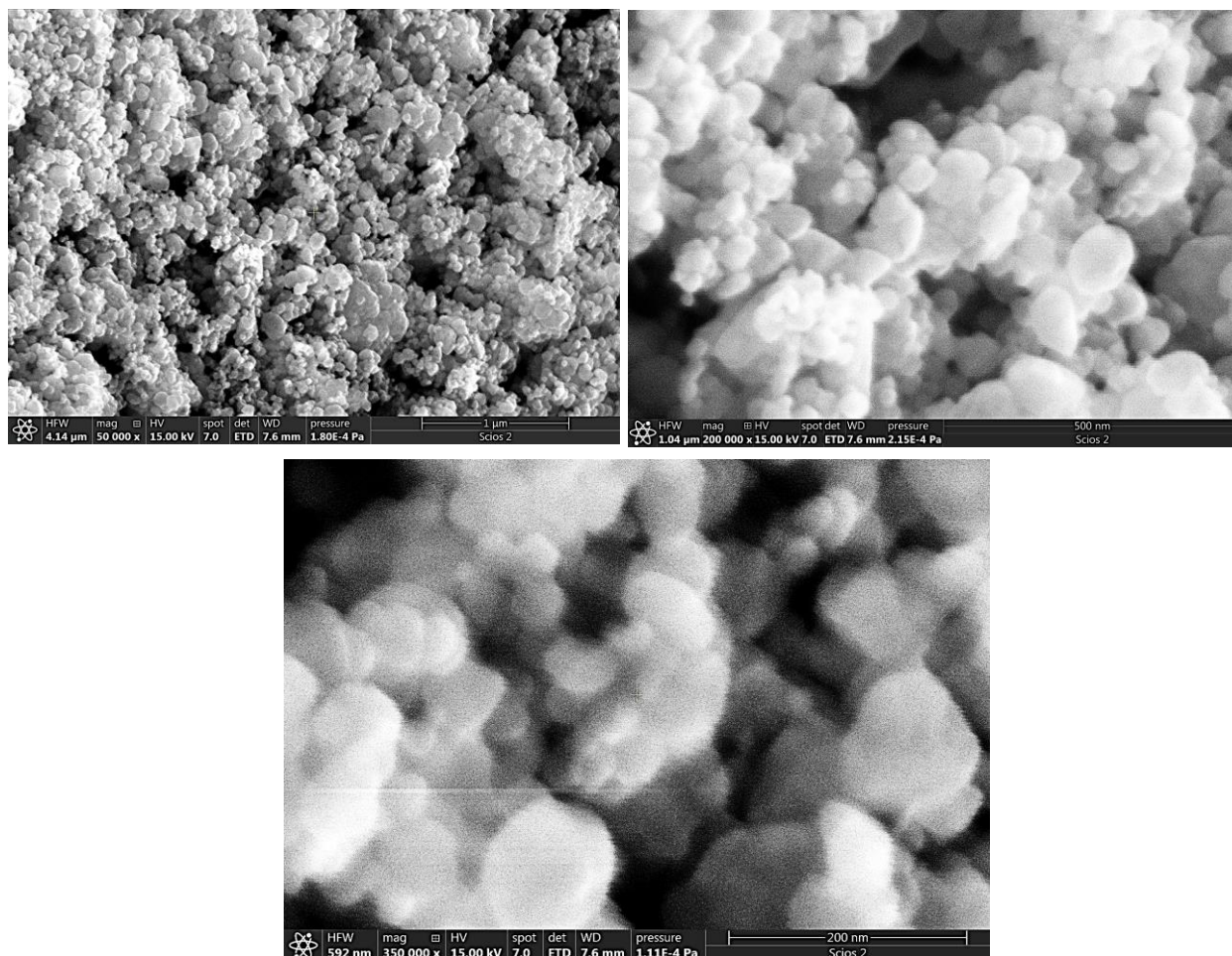


Figure 23: SEM images at different scales (1  $\mu\text{m}$ , 500 nm, and 200 nm)

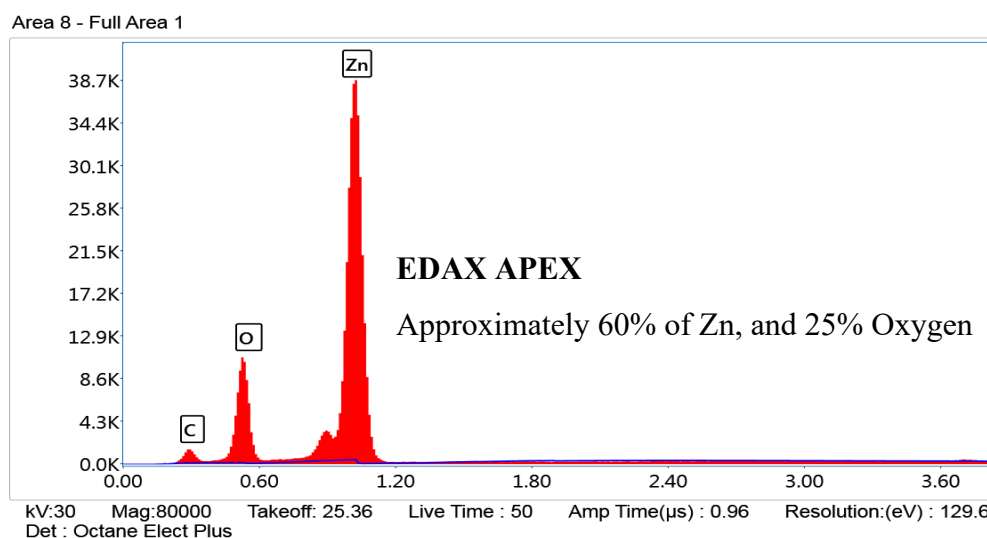


Figure 24: composition of ZnO Nanoparticles

### III.3. Photodegradation result of Methylene blue

#### III.3.1 Visible Absorbance Spectrum of Methylene Blue

The UV-Vis absorption spectrum of methylene blue (MB) dye was detected, it was scanned from 550 to 750 nm. Based on this result, the maximum absorption wavelength of methylene blue (MB) was detected at 664nm. (figure23)

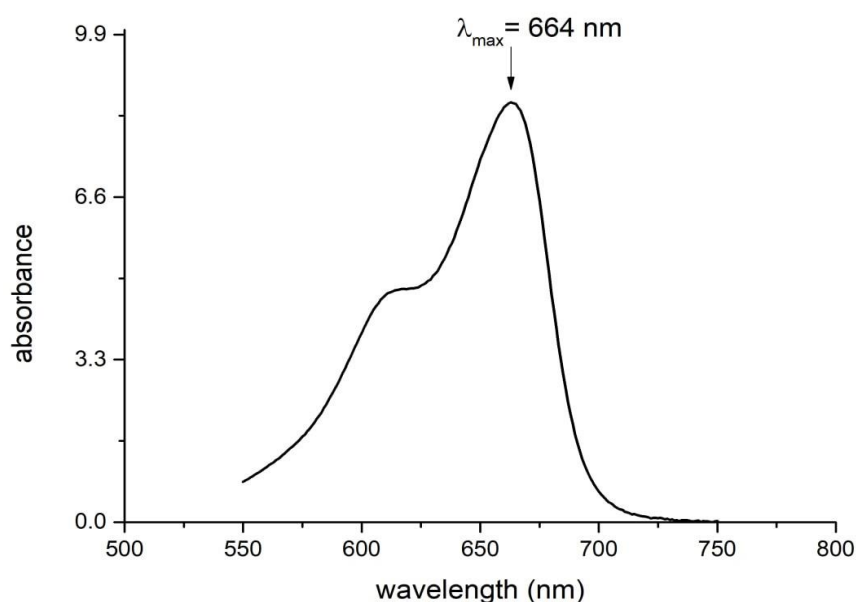


Figure 25:UV-Vis absorption spectra of the MB solution

### III.3.2 Evolution of photodegradation over time

The effect of UV radiation exposure time was monitored for **ZnO-NPs** (figure 24):

The figure below shows the degradation curves of methylene blue for the control sample and the ZnO NPs solution. Both curves show a decrease with irradiation time under UV light, however the faster decreasing for the ZnO NPs solution confirms that ZnO nanoparticles have a photocatalytic activity that is helpful in degrading methylene blue over time. A nearly constant region observed between 100 and 120 min in the ZnO NPs curve may indicate a temporary stabilization of the degradation process, possibly due to saturation of active sites on the catalyst surface, electron-hole pair recombination, or minor experimental fluctuations during measurement.

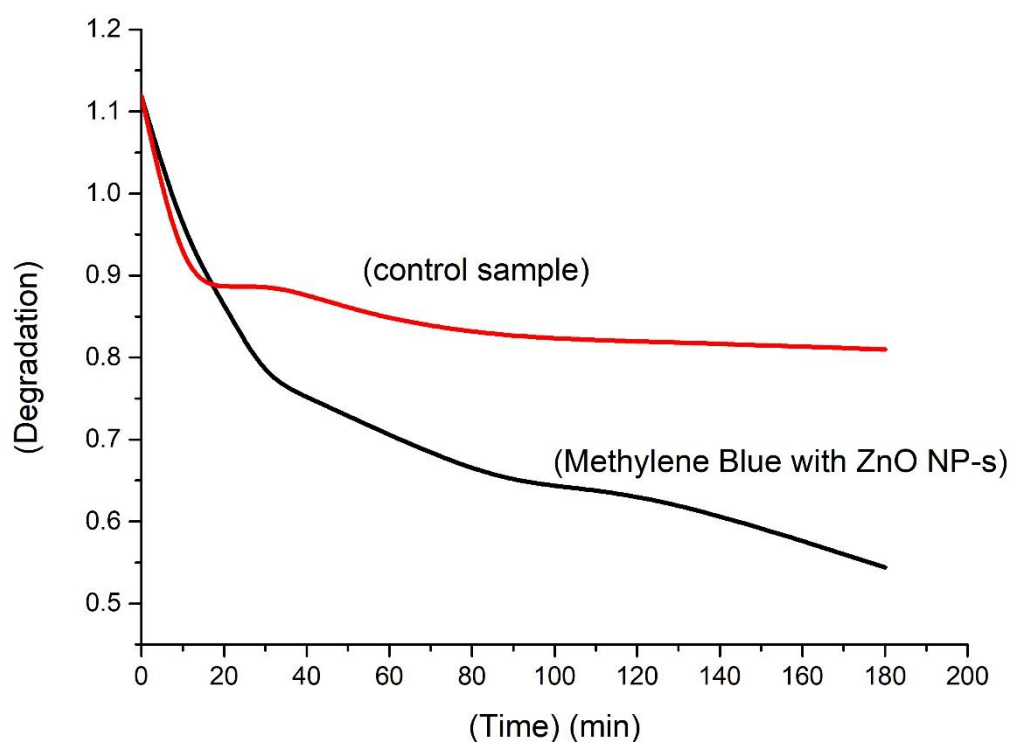


**Figure 26: Photodegradation of methylene blue and its control over time**

### III.4. Design of experiments

A total of 15 duplicated experimental tests were conducted in the laboratory to validate the model. The average response showed a deviation of approximately 2.7 % between the predicted

and experimental responses. This allowed us to demonstrate consistency between the model and the experimental results of Methylene Blue photodegradation.

The operating conditions were optimized using statgraphics software. The optimal values are:

PH of the solution (PH)= 10.99,

The temperature (T)= 40°C,

And the mass of nanoparticles= 0.1g.

### III.4.1 Experience Matrix

The data of the matrix used in this study are illustrated in Table 6:

**Table 6: Experience and response matrix**

| Nbr | PH | T  | M    | %     |
|-----|----|----|------|-------|
| 1   | 7  | 30 | 0.1  | 49.04 |
| 1   | 3  | 20 | 0.1  | 40.42 |
| 1   | 11 | 20 | 0.1  | 48.73 |
| 1   | 3  | 40 | 0.1  | 79.31 |
| 1   | 11 | 40 | 0.1  | 87.59 |
| 1   | 3  | 30 | 0.05 | 33.18 |
| 1   | 11 | 30 | 0.05 | 36    |
| 1   | 7  | 30 | 0.1  | 47.66 |
| 1   | 3  | 30 | 0.15 | 43.13 |
| 1   | 11 | 30 | 0.15 | 43.35 |
| 1   | 7  | 20 | 0.05 | 21.02 |
| 1   | 7  | 40 | 0.05 | 62.23 |
| 1   | 7  | 20 | 0.15 | 33.6  |
| 1   | 7  | 40 | 0.15 | 64.55 |
| 1   | 7  | 30 | 0.1  | 50    |

Table 7: Levels table

| Levels     | PH | T  | Mass |
|------------|----|----|------|
| Low level  | 3  | 20 | 0.05 |
| High level | 11 | 40 | 0.15 |

### III.4.2 Analysis of variance (ANOVA)

The box-behnken design mathematical model was evaluated using ANOVA statistical tests. The error between the experimental value and the calculated value is very low. The results obtained using statgraphics software are presented in the table. Model terms with a significant p-value ( $p \leq 0.05$ ) means that the test hypothesis should be rejected, and greater than ( $p > 0.05$ ) means that no effect was observed. From these results, we can see that the model's value less than 0.05, The analysis indicates that temperature, temperature<sup>2</sup>, PH, PH<sup>2</sup>, and mass, mass<sup>2</sup> are all statistically significant factors in the model. Examination of the interaction between the various parameters selected, namely the PH (a), the temperature (b), and the mass of nanoparticles (c), shows no effect on the result.

Table 8: Analysis of Variance for removal (ANOVA):

| Source        | Sum of Squares | Df | Mean Square | F-Ratio | P-Value |
|---------------|----------------|----|-------------|---------|---------|
| A:ph          | 48.1671        | 1  | 48.1671     | 7.94    | 0.0372  |
| B:T           | 2809.13        | 1  | 2809.13     | 462.89  | 0.0000  |
| C:m           | 129.605        | 1  | 129.605     | 21.36   | 0.0057  |
| AA            | 69.5068        | 1  | 69.5068     | 11.45   | 0.0196  |
| AB            | 0.000225       | 1  | 0.000225    | 0.00    | 0.9954  |
| AC            | 1.69           | 1  | 1.69        | 0.28    | 0.6203  |
| BB            | 428.58         | 1  | 428.58      | 70.62   | 0.0004  |
| BC            | 26.3169        | 1  | 26.3169     | 4.34    | 0.0918  |
| CC            | 757.55         | 1  | 757.55      | 124.83  | 0.0001  |
| Total error   | 30.3435        | 5  | 6.0687      |         |         |
| Total (corr.) | 4405.36        | 14 |             |         |         |

### III.4.3 Mathematical model

$$\text{Removal} = 15.5915 - 2.85234 \cdot \text{pH} - 4.07606 \cdot T + 1403.05 \cdot m + 0.271172 \cdot \text{pH}^2 - 0.0001875 \cdot \text{pH} \cdot T - 3.25 \cdot \text{pH} \cdot m + 0.107737 \cdot T^2 - 5.13 \cdot T \cdot m - 5729.5 \cdot m^2$$

The response (removal) represented in two parts: a quadratic part, and linear part as a function of three factors: pH of the solution(ph), The temperature (T), And the mass of nanoparticles.

### III.4.4 Main Effects Plots interpretation

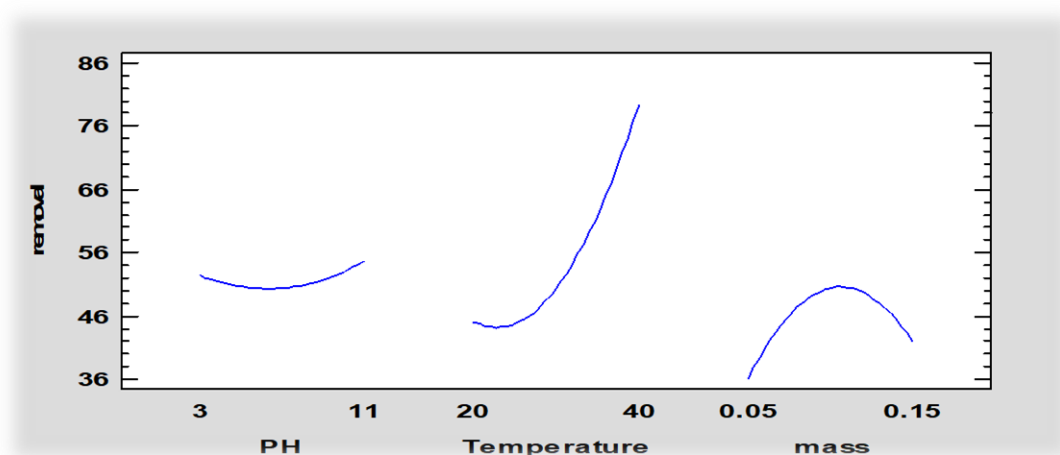


Figure 27 : main effects plots

#### III.4.4.1 Effect of ph

A maximum elimination rate with basic ph, where removal is maximized, can be seen from curves. The response first declines, reaches a minimum at pH 5–6, and then rises once more to the optimal level. Similar behavior was reported by A.F. ALKAIM and others[50]. Obtained similar results in the presence of ZnO, the photodegradation was significantly enhanced at high pH (pH = 10.99). While the lowest degradation efficiencies at acidic pH were attributed to the photocorrosion (photodecomposition) and dissolution of ZnO into  $\text{Zn}^{2+}$  ions in acidic and near-neutral solutions.

#### III.4.4.2 Effect of Temperature (T)

According to the main effect plots Removal increases significantly with temperature, indicating a great efficiency at higher temperatures, most likely as a result of increased photocatalytic activity.

### III.4.4.3 Effect of mass of ZnO NPs

There is an optimal catalyst dose which is around 0.08–0.1 g, more than this, the performance drops, possibly because too many ZnO particles lead to light scattering or agglomeration. Less than that, also not so good performance because of the lack of the amount of the catalyst (ZnO NPs), reducing effective surface area. According to Azad Kumar and others [51], Degradation of methylene blue is affected by the amount of the catalyst. The photodegradation of dye increases with increasing catalyst (ZnO NPs) amount, which is the feature of heterogeneous photocatalysis. The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the formation of number of OH radicals which can take part in actual discoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing.

### III.4.5 Interaction plots

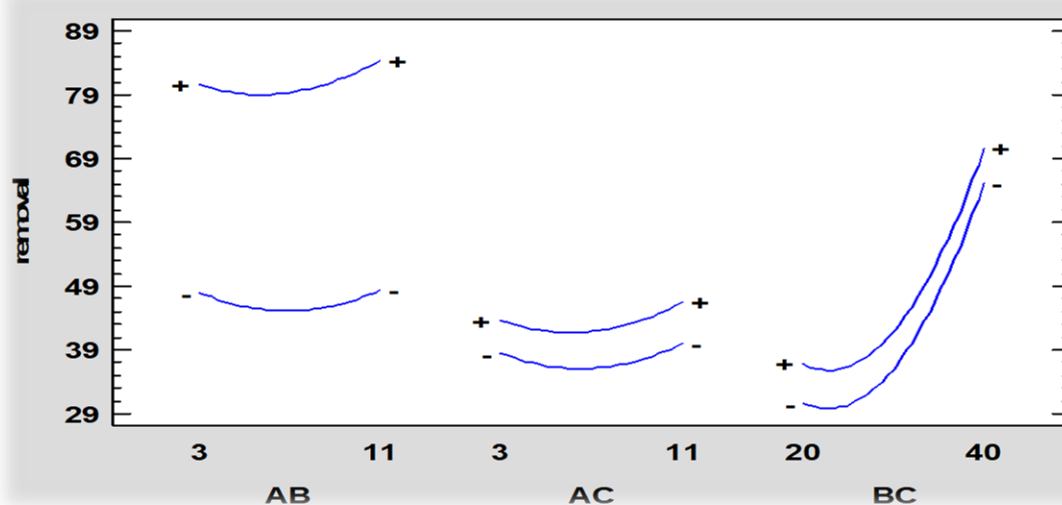


Figure 28: Interaction plots

The Interaction Plots shows that the interaction between all the factors has no effect on the results. (figure 27)

### III.4.6 Response Surface and Contour Plot Optimization

These results were obtained by varying two parameters in the experimental domain, while the third parameter was kept constant (at the central level = 0). (Figure)

Because of unfavorable surface charge or reaction kinetics, removal efficiency is low in acidic media, particularly at lower temperatures.

This implies that neutral to basic conditions are more conducive to the process of photocatalysis degradation.

Across all pH levels, removal is typically higher at higher temperatures ( $\sim 35\text{--}40^\circ\text{C}$ ).

Implies that the process is thermally activated or endothermic (removal is accelerated by higher temperatures).

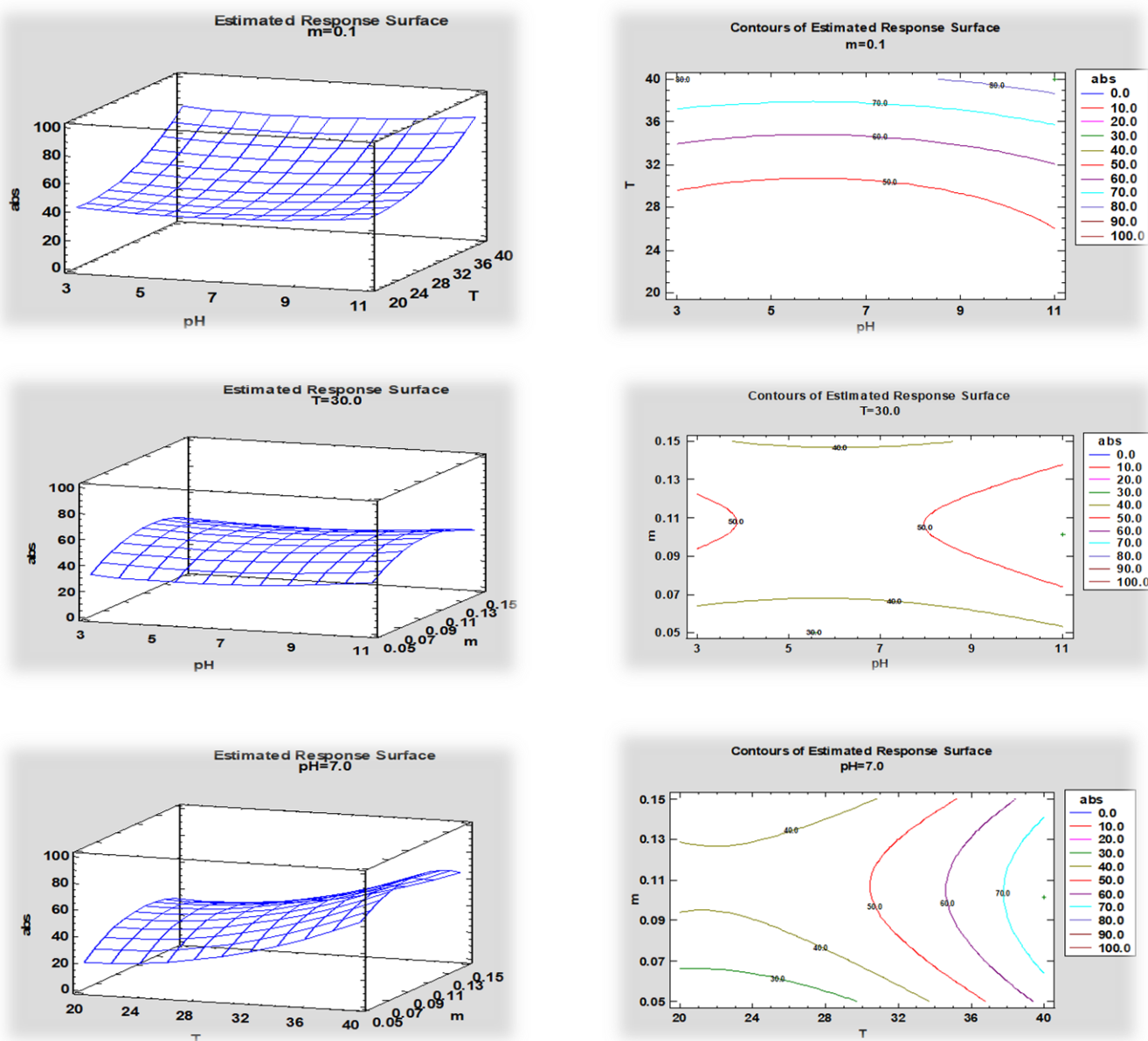


Figure 29: Response surface and countour plots

#### **III.4.6.1 Removal Efficiency as a Function of pH and Temperature**

High removal rates ( $\geq 80\%$ ) are observed at elevated temperatures ( $T \geq 35\text{ }^{\circ}\text{C}$ ). However, at lower temperatures ( $T < 28\text{ }^{\circ}\text{C}$ ), the efficiency drops below 60%, particularly under acidic to neutral pH conditions. The lightest regions of the contour plot—representing low pH and low temperature—indicate the lowest removal efficiencies ( $< 40\%$ ).

#### **III.4.6.2 Removal Efficiency as a Function of Temperature and Catalyst Mass**

The highest removal efficiencies ( $> 90\%$ ) are achieved at  $40\text{ }^{\circ}\text{C}$  and a catalyst mass around 0.10 g. Temperature demonstrates a more significant positive impact on dye removal than catalyst mass. At lower temperatures ( $\leq 25\text{ }^{\circ}\text{C}$ ), removal rates remain below 50%, regardless of the amount of ZnO used. Increasing the catalyst mass alone has minimal effect unless combined with elevated temperatures, highlighting temperature as a key factor in optimizing removal efficiency.

#### **III.4.6.3 Removal Efficiency as a Function of pH and Catalyst Mass**

Removal efficiency is limited at lower pH values (3–5), especially when the catalyst mass is less than 0.08 g. Although performance is improved by increasing ZnO mass, the improvement occurs more strongly at higher pH values. Overall, neither low catalyst dosages nor extremely acidic environments produce effective degradation.

According to these findings, temperature has the biggest influence on dye removal efficiency, followed by catalyst mass, while pH has the least impact. This trend aligns with the observations from the main effects plot.

### III.5. Photodegradation of Fast Blue R134 and its control over time using optimal conditions

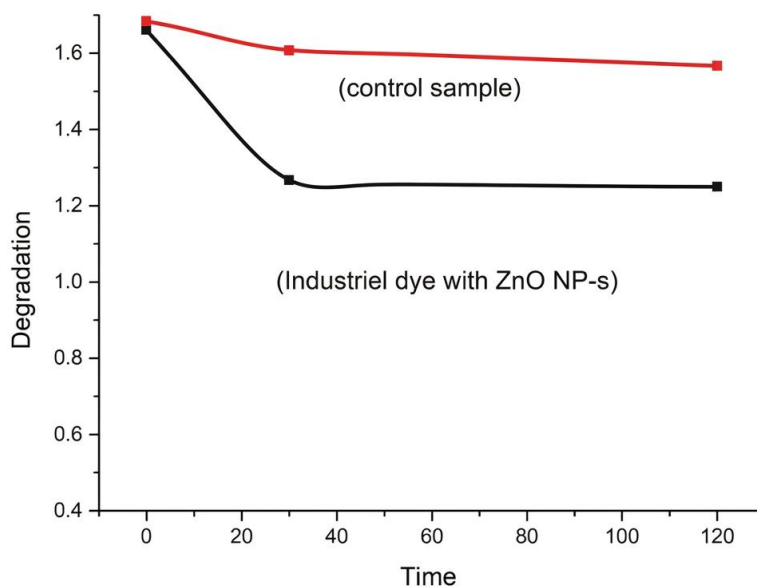


Figure 30: Photodegradation of Fast Blue R134 and its control over time

### III.6. Long-Term UV and Sunlight Exposure on Dye Degradation Efficiency

To examine the effect of prolonged exposure on the photodegradation process, two dye-contaminated wastewater samples—industrial dye-contaminated wastewater and methylene blue dye-contaminated wastewater—were tested alongside their respective controls. The experiment was carried out continuously over approximately three consecutive days (over the weekend). During this period, each sample was exposed to ultraviolet (UV) radiation for a total of two hours, followed by exposure to natural sunlight for the remainder of the experimental duration (approximately 30 hours). Visual observation revealed a complete loss of color in the dye-containing samples (figure 29), indicating substantial degradation. These observations were confirmed by the experimental results, which showed near-total photodegradation (~100%) in both dye-contaminated samples, while the control samples exhibited minimal to no degradation.

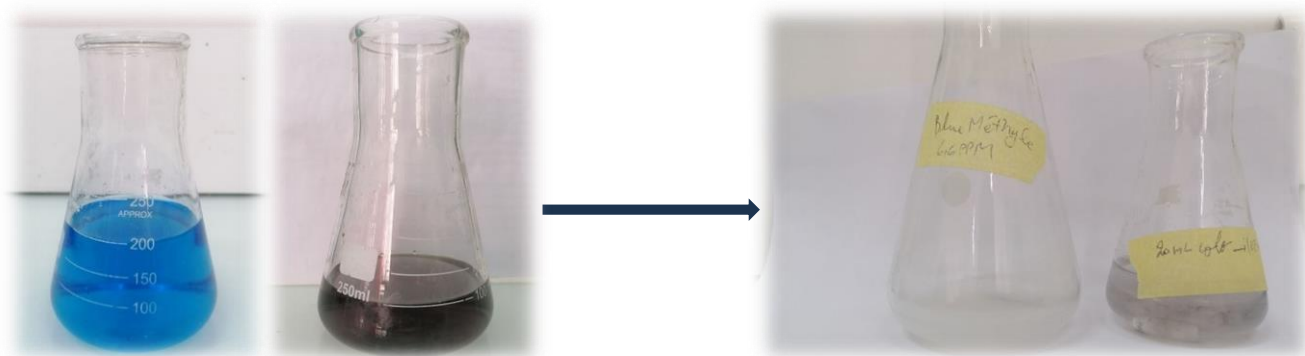


**Figure 31: Effect of UV and Sunlight Irradiation on Methylene Blue and Industrial Dye Solutions**

## GENERAL CONCLUSION

This research successfully demonstrated the synthesis of efficient zinc oxide nanoparticles (ZnO NPs) using an environmentally friendly green chemistry approach, employing orange leaf extract as a natural reducing and stabilizing agent for the treatment of dye-contaminated wastewater. The synthesized ZnO nanoparticles exhibited a wurtzite crystalline structure with a band gap of 3.31 eV. These nanoparticles were applied for the removal of methylene blue dye from synthetic wastewater and Fast Blue R134 from real industrial effluent.

To optimize the conditions for dye degradation and to better understand the influence of key variables, a Box–Behnken Design (BBD) of experiments was employed. Three factors were examined: ZnO nanoparticle mass, solution temperature, and pH. The optimal conditions for methylene blue degradation were identified as a ZnO mass of 0.1 g, temperature of 40 °C, and pH 11. Among these, temperature emerged as the most influential factor. Under optimal conditions, the process achieved a maximum removal efficiency of 91.32%, attributed to the ZnO NPs favorable properties, including small crystal size, high crystallinity, low band gap energy, and multi-structured morphology.

Additionally, visual observation confirmed complete color removal in dye-containing solutions, further supporting the photocatalytic activity of the synthesized ZnO. These findings validate the potential of ZnO nanoparticles derived from renewable plant-based sources as effective photocatalysts for the degradation of organic dyes in aqueous environments. Overall, this work contributes to the advancement of green nanotechnology and presents a sustainable, low-cost method for producing photocatalysts suitable for future applications in wastewater treatment.

Based on the findings of this study, several recommendations can be made to guide future research. Firstly, further investigations should be conducted to evaluate the effect of prolonged exposure to ultraviolet (UV) radiation on the efficiency of the photodegradation process. This could provide deeper insights into the kinetics and long-term stability of ZnO nanoparticles under extended irradiation. Secondly, additional studies should explore the degradation of a wider range of dye types and colors, particularly those commonly used in various industrial sectors, to assess the broader applicability of the synthesized photocatalyst. Finally, special

attention should be given to the characterization and treatment of real industrial wastewater, as it may contain complex mixtures of organic and inorganic contaminants. A more comprehensive understanding of these real-world matrices is essential for developing effective and scalable treatment strategies using green-synthesized ZnO nanoparticles.

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## Annex

## Authorization for final printing of a master's thesis

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## Autorisation d'impression finale d'un mémoire de master

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| Co-encadrant | Khan Yasmine    | [Signature] |

Soussigne Mr: Bentoufa DjehadPrésident de jury des étudiant (s): ALISA BAKIR - ALISMAL JAKHUEL

Fillère : Génie des procédés ; Spécialité : Génie chimique

Thème: Treatment of organic waste water Effluents using synthesized ZnO nanoparticles: A Comparative study of chemical and physical approach.  
Autorise le (s) étudiant (s) mentionné (s) ci-dessus à imprimer et déposer leur (s) manuscrit final au niveau du département.

Ghardaïa le: 06 أكتوبر 2026

Président de jury

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Le chef de département

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