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GREEN SYNTHESIS OF Pd-MCM41 NANOCMPOSITE FOR ENVIRONMENTAL APPLICATION

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COMMON ABBREVIATIONS AND THEIR MEANINGS

BOD : Biochemical Oxygen Demand

UV : Ultraviolet

MBRs : Membrane Bioreactors

RO : Reverse Osmosis

AOPs : Advanced Oxidation Processes

VOCs : Volatile Organic Compounds

OH : Hydroxyl (often referring to the hydroxyl radical, •OH)

SO4 : Sulfate (often referring to the sulfate radical, •SO4−)

PdNPs : Palladium Nanoparticles

FCC : Fluid Catalytic Cracking

HCP : Hexagonal Close-Packed

SPR : Surface Plasmon Resonance

SERS : Surface-Enhanced Raman Spectroscopy

LEDs : Light-Emitting Diodes

IUPAC : International Union of Pure and Applied Chemistry

FSM-16 : Folded Sheet Mesoporous Material-16 (a type of mesoporous silica)

M41S : A family of mesoporous silicates (includes MCM-41, MCM-48, MCM-50)

MCM-41 : Mobil Composition of Matter No. 41 (a type of mesoporous silica)

MCM-48 : Mobil Composition of Matter No. 48 (a type of mesoporous silica)

MCM-50 : Mobil Composition of Matter No. 50 (a type of mesoporous silica)

SBA : Santa Barbara Amorphous (a family of mesoporous silicas, e.g., SBA-15)

MOFs : Metal-Organic Frameworks

CTAB : Cetyltrimethylammonium Bromide

TEOS : Tetraethyl Orthosilicate

MEMs : Microelectromechanical Systems

PCB : Printed Circuit Board

HF : Hydrofluoric acid

MSNs : Mesoporous Silica Nanoparticles

TiO2 : Titanium Dioxide

KIT-6 : Korea Advanced Institute of Science and Technology No. 6 (a type of mesoporous silica)

NaOH : Sodium Hydroxide

NH4OH : Ammonium Hydroxide

FTIR: Fourier-Transform Infrared (Spectroscopy)

TEM: Transmission Electron Microscopy

XRD: X-ray Diffraction

NaCl: Sodium Chloride

Mg: Milligram

SEM: Scanning Electron Microscopy

USA: United States of America

SPR: Surface Plasmon Resonance

PH: Potential of Hydrogen (a measure of acidity or alkalinity)

T°: Temperature

MB: Methylene Blue

GENERAL INTRODUCTION

I.1.1. General Introduction

Water pollution caused by synthetic dyes, commonly discharged by industries such as textiles, cosmetics, and paper production, poses a serious environmental and health threat due to their chemical stability, toxicity, and resistance to degradation. These pollutants not only affect aquatic ecosystems but also endanger human and animal life. Therefore, the development of efficient, eco-friendly, and sustainable treatment methods for dye-contaminated wastewater has become a critical area of research.

In this context, the present study aims to develop a novel photocatalytic system based on palladium nanoparticles supported on mesoporous silica (MCM-41) for the degradation of methylene blue dye. To minimize environmental impact during synthesis, the nanoparticles are prepared using a green chemistry approach involving *Lawsonia inermis* (henna) leaf extract, serving as a natural reducing and stabilizing agent.

This work is structured as follows :

- **Chapter I** presents a literature review on dye pollution, treatment methods, advanced oxidation processes (AOPs), and the roles of palladium nanoparticles, mesoporous materials, and *Lawsonia inermis* in green synthesis.
- **Chapter II** details the materials, biosynthesis process of Pd-MCM-41, and characterization techniques (UV-Vis, XRD, TEM, FTIR), along with tests to optimize synthesis and degradation conditions.
- **Chapter III** discusses the results, including the effect of various parameters on nanoparticle formation and dye degradation efficiency.

By integrating green synthesis, nanotechnology, and advanced photocatalytic methods, this study offers an innovative and sustainable strategy for addressing the pressing issue of dye pollution in wastewater, with implications for both scientific research and environmental protection.

I.Genral information of dyes

I.1.1. Introduction

Colored organic compounds known as dyes impart color to materials by selectively absorbing light. They are commonly used in industries such as textiles, food, cosmetics, and biology.[1]

Their coloring function arises from their ability to absorb specific wavelengths of visible light—a property that results from their conjugated molecular structures and chromophore groups.[2]

Dye chemistry encompasses various classes, including azo, anthraquinone, and phthalocyanine dyes, each defined by unique structural characteristics and synthesis methods.[3]

Azo dyes, which are distinguished by the presence of an –N=N– azo group, form the largest class and are typically synthesized through diazotization and coupling reactions.[4]

Historically, natural dyes derived from plants and animals were widely used, until William Henry Perkin's synthesis of mauveine in 1856 marked the beginning of synthetic dye chemistry .[5]

Beyond simple coloration, modern dye chemistry has advanced to include complex dyes used in electronics, medicine, and solar cells, highlighting its broader significance.[6]

I.1.2. Definition

Dyes are organic compounds that contain a chromophore group (responsible for color) and auxochrome groups (which influence solubility and the dye's ability to bind to a substrate)."[7] They are defined as substances that can permanently impart color to other materials—especially fabrics—through chemical bonding or physical absorption.[8]

I.1.3. Classification of Dyes

I.1.3.a Classification Based on Application Method

It is the most common and useful way to categorize dyes since it demonstrates their behavior with various substrates such as cotton, wool, and polyester.

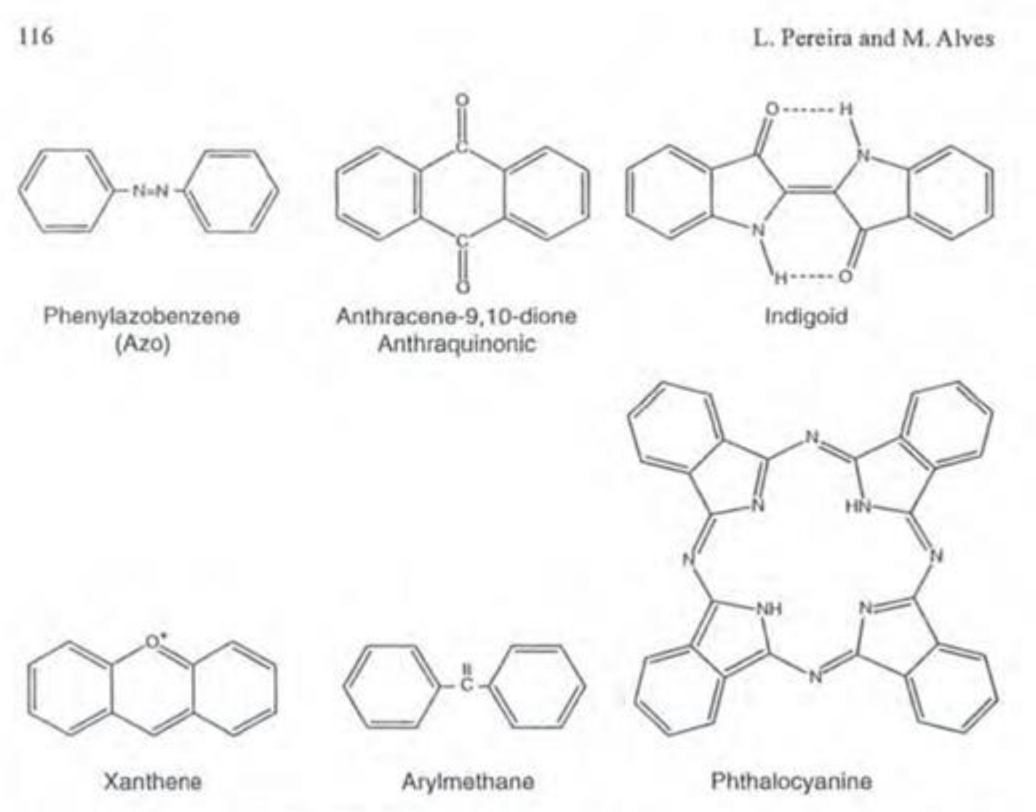
Table I.1:classification of dyes based on application method

Type of Dye	Description	Substrate
Direct dyes	Water-soluble dyes that are applied directly to the fabric, usually cotton.	Cellulose (cotton)
Reactive dyes	Form covalent bonds with fiber, ensuring excellent wash fastness.	Cotton, wool, silk
Disperse dyes	Poorly water-soluble dyes used for synthetic fibers.	Polyester, nylon
Acid dyes	Anionic dyes applied under acidic conditions.	Wool, silk, nylon
Basic dyes	Cationic dyes, bright but with poor fastness unless modified.	Acrylics, modified nylons
Vat dyes	Insoluble dyes that become soluble when reduced, then oxidized back in the fiber.	Cotton
Sulfur dyes	Economical dyes mainly for deep shades on cotton.	Cotton
Azoic dyes	Dyes formed directly on the fiber via a diazo-coupling reaction.	Cellulose fibers
Mordant dyes	Require a metal salt (mordant) to fix to the fiber.	Wool, silk [9]

I.1.3.b Classification Based on Chemical Structure

Table I.2:classification of dyes based on chemical structure

Chemical Class	Key Features
Azo dyes	Contain one or more azo (-N=N-) groups. Largest class of synthetic dyes.
Anthraquinone dyes	Based on anthraquinone structure, often used for blue and green shades.
Indigoid dyes	Include indigo, traditionally used for denim.
Triarylmethane dyes	Bright colors but low light fastness. Used in paper and ink.
Phthalocyanine dyes	Contain copper or other metal complexes. Used for brilliant blues and greens.
Nitro and nitroso dyes	Rare, used for specialized yellow/orange shades. [10]



FigureI.1 : Different chromophores : Azo, anthraquinonic, indigoid, xanthene, arylmethane and phthalocyanine dye structures

I.1.3.c .Classification Based on Origin

Table I.3:classification of dyes based on their origin

Type	Source
Natural dyes	Derived from plants (e.g., indigo), insects (e.g., cochineal), or minerals.
Synthetic dyes	Man-made, mainly from petrochemical sources. Dominant in modern industry. [11]

I.1.4 Toxicity and environmental impact

Environmental pollution remains a critical challenge in the modern world, with industries acting as major contributors. Among them, the textile industry is particularly notorious for generating large volumes of liquid effluents, largely due to the vast quantities of water used during fabric processing. [12] These discharges directly contaminate nearby surface and groundwater sources. It is estimated that approximately 280,000 tons of textile dyes are released into wastewater streams globally each year..[13]

Synthetic dyes present a significant ecological threat, particularly in aquatic environments. Their presence in industrial effluents reduces light penetration in water bodies, which hinders photosynthesis in aquatic plants and disrupts the entire aquatic food chain. Moreover, dye particles can accumulate as a thin film on the surface of water, decreasing dissolved oxygen levels and endangering aquatic organisms.

Additionally, the presence of dyes in wastewater leads to an increase in biochemical oxygen demand (BOD), further stressing aquatic ecosystems. Many of these dyes are chemically stable and resistant to degradation, allowing them to persist in the environment for extended periods.

There is also growing concern over their xenobiotic nature—meaning they are foreign to biological systems. These compounds can be toxic, mutagenic, or even carcinogenic, posing serious health risks to both aquatic life and humans who rely on contaminated water sources[14]

***Table I.4* : Colour concentrations limits and quantum of water generated from industries**

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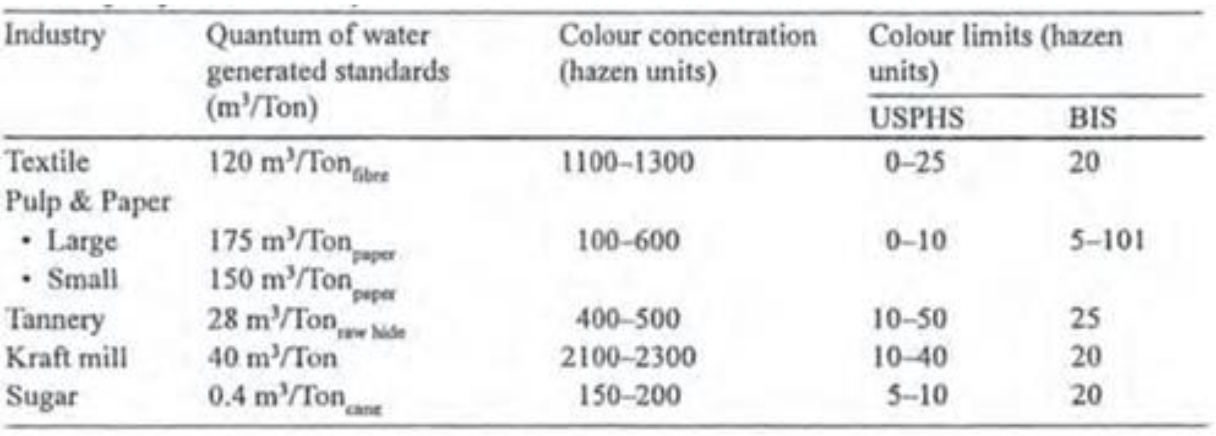


Industry	Quantum of water generated standards (m^3/Ton)	Colour concentration (hazen units)	Colour limits (hazen units)	
			USPHS	BIS
Textile	120 m^3/Ton_{fibre}	1100–1300	0–25	20
Pulp & Paper				
• Large	175 m^3/Ton_{paper}	100–600	0–10	5–101
• Small	150 m^3/Ton_{paper}			
Tannery	28 $m^3/Ton_{raw\ hide}$	400–500	10–50	25
Kraft mill	40 m^3/Ton	2100–2300	10–40	20
Sugar	0.4 m^3/Ton_{cane}	150–200	5–10	20

I.2. Water treatment

Water treatment is a critical process aimed at improving the quality of water to make it suitable for various intended uses, such as drinking, industrial applications, or environmental protection [16] the primary objective is to eliminate or significantly reduce harmful contaminants, including suspended solids, pathogenic microorganisms, heavy metals, and chemical pollutants.[17]

Water treatment generally involves a combination of physical, chemical, and biological methods.[18]

Physical treatment methods, such as sedimentation and filtration, are used to remove solid particles and reduce turbidity . Chemical treatment employs coagulants like alum to aggregate fine particles into larger flocs, facilitating their removal. Disinfectants such as chlorine and ozone are then used to eliminate harmful microorganisms..[19]
Biological treatment is particularly effective for wastewater and surface water sources, where microbial communities break down organic matter through natural degradation processes. [20]

A conventional drinking water treatment train typically includes coagulation, flocculation, sedimentation, filtration, and disinfection.[21]
. In cases where water is contaminated with specific or hazardous substances, advanced treatment technologies—such as reverse osmosis (RO), ultraviolet (UV) disinfection, and activated carbon filtration—are implemented.[22]

Effective water treatment is essential for preventing waterborne diseases such as cholera, typhoid, and hepatitis A. Furthermore[23], it plays a pivotal role in promoting the sustainable management of water resources, enabling water reuse and safeguarding aquatic ecosystems from degradation. [24]

1.2.1Wastewater Treatment :

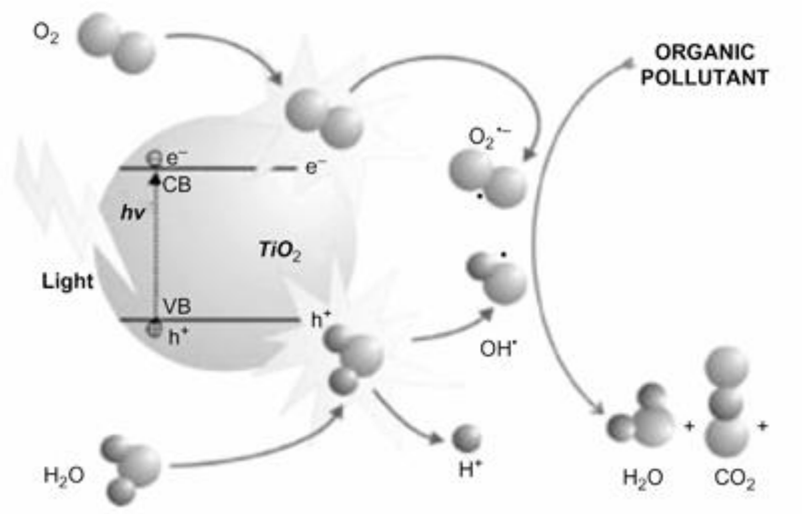
Wastewater treatment is a critical process designed to remove contaminants from used or polluted water, making it safe for either environmental discharge or reuse.[25]
This process plays a fundamental role in safeguarding public health and preserving environmental integrity, particularly against pollutants originating from domestic, industrial, and agricultural sources[26]

This stage focuses on the physical separation of coarse materials to reduce the initial load on subsequent processes [27]
Next, secondary treatment employs biological methods, such as the activated sludge process, in which microorganisms metabolize and break down dissolved and suspended organic

matter. This stage significantly reduces the biochemical oxygen demand (BOD) of the effluent.[28]

In many modern treatment facilities, a tertiary (or advanced) treatment stage is implemented to further purify the water.[29]
This step targets the removal of nutrients such as nitrogen and phosphorus, along with any remaining suspended solids and pathogens [30]

Final disinfection, using agents such as chlorine, ultraviolet (UV) light, or ozone, ensures the elimination of disease-causing microorganisms before the treated water is safely discharged into the environment or reused.[31]
The sludge generated throughout the treatment process is subjected to additional treatment methods, including thickening, anaerobic or aerobic digestion, and dewatering, to minimize volume and enhance safety for disposal or reuse [32]. When processed to meet regulatory standards, treated sludge—referred to as biosolids—can be beneficially applied in agriculture as a soil amendment.With increasing demand for water reuse [33], particularly in water-scarce regions, advanced technologies such as membrane bioreactors (MBRs) and reverse osmosis (RO) are being adopted to achieve higher levels of water purification. [34]



***FigureI.2*: Mechanism of Photocatalytic Degradation of Organic Pollutants on TiO_2[35]**

I.3. Advanced Oxidation Processes (AOPs)

I.3.1 Introduction

Advanced Oxidation Processes (AOPs) represent an environmentally friendly and highly effective strategy for the degradation of a wide variety of pollutants, including both airborne contaminants and a broad spectrum of waterborne pollutants. These pollutants encompass aromatic compounds.[36]

petroleum derivatives, chlorinated hydrocarbons, pesticides, insecticides, volatile organic compounds (VOCs), dyes, and numerous other organic substances that are resistant to conventional treatment methods., AOPs operate by generating highly reactive species—primarily hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet -}$)—which possess strong oxidizing capabilities. These radicals are capable of attacking and decomposing complex organic molecules, often leading to their complete mineralization into harmless end-products such as carbon dioxide and water. [37].

The concept of AOPs was first introduced in the 1980s, initially for the treatment of drinking water. Since then, the technology has evolved and gained widespread application in the treatment of various types of industrial and municipal wastewaters, [38] owing to its proven effectiveness in degrading recalcitrant organic pollutants and in removing certain inorganic contaminants. This thesis aims to explore both the fundamental principles and the latest advancements in AOP technologies[39], with a particular emphasis on their application in the treatment of landfill leachate—a highly complex and challenging waste stream. Through this study, the effectiveness[40], mechanisms, and limitations of AOPs will be critically assessed, highlighting their potential as a sustainable solution for advanced wastewater treatment [41]

I.3.2 Heterogeneous AOPs

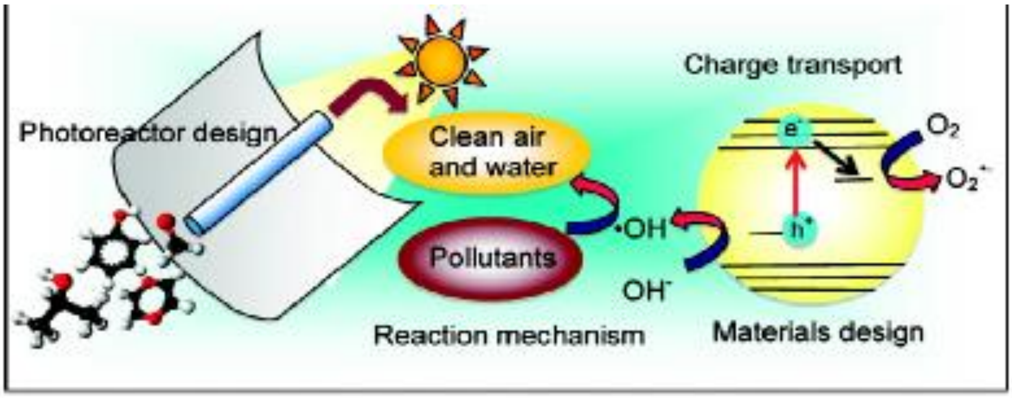
Advanced Oxidation Processes (AOPs) are considered an environmentally sustainable and highly efficient technology for the removal of a wide range of pollutants, including airborne and waterborne contaminants. [42] These include aromatic compounds, petroleum-based substances, petroleum hydrocarbons, chlorinated hydrocarbons, pesticides, insecticides, volatile organic compounds (VOCs), dyes, and various other persistent organic pollutants [43]

AOPs function by generating powerful oxidizing radicals, predominantly hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{•-}$),[44]. which are capable of decomposing even the most stable and hazardous organic compounds into less harmful or fully mineralized products. This technology was first introduced in the 1980s, primarily for the treatment of drinking water. Due to their remarkable efficacy, AOPs were subsequently adopted for the treatment of diverse wastewater streams, particularly those containing recalcitrant organic and inorganic pollutants. [45] The objective of this thesis is to provide a comprehensive review of the fundamental principles and recent developments in AOP technologies, with a specific focus on their application in landfill leachate treatment. [46] This waste stream presents a significant environmental challenge due to its complex composition, making it an ideal candidate for advanced treatment approaches like AOPs. [47]

I.4. Photocatalysis

Catalysis plays a crucial role in various industrial and environmental processes. In the chemical and petroleum industries, many essential reactions rely on catalysts to achieve efficient and selective transformations. Additionally, in environmental chemistry, catalysts are indispensable for the degradation of pollutants, such as those found in automobile exhaust and industrial emissions.[48].

A catalyst is defined as a substance that accelerates the rate of a chemical reaction without undergoing any permanent chemical change itself. Catalysts function by providing an alternative reaction pathway that has a lower activation energy, thereby facilitating the conversion of reactants into products more efficiently.[49]



FigureI.3: **Schematic of the interplay of photocatalysis treatment, reactor and material design and photocatalytic reaction mechanism.**[50]

I.5. Palladium Nanoparticle:

I.5.1 Introduction to palladiums nanoparticles

Palladium nanoparticles (PdNPs) have garnered significant interest in recent years due to their unique catalytic, electronic, and optical properties. [51] These properties differ markedly from those of bulk palladium, primarily because of the high surface-area-to-volume ratio and quantum size effects that dominate at the nanoscale. PdNPs find extensive applications in various catalytic processes, including hydrogenation, carbon–carbon coupling, and environmental remediation [52]

Their exceptional performance in cross-coupling reactions, such as the Suzuki and Heck reactions, has established them as indispensable catalysts in synthetic organic chemistry. Furthermore, owing to their excellent electrocatalytic properties, palladium nanoparticles are being actively explored for applications in fuel cells, hydrogen storage, and biosensors.[53] Recent advances in green synthesis methods have enabled the fabrication of PdNPs using plant extracts, microorganisms, and other eco-friendly techniques, [54] significantly reducing the reliance on toxic chemicals. Despite these developments, challenges remain in achieving precise control over the size, shape, and distribution of PdNPs—factors that are critical to optimizing their catalytic efficiency. [55]

I.5.3 Properties of Palladiums

I.5.3.a Structural Properties

Palladium nanoparticles (PdNPs) exhibit unique structural characteristics—including size, shape, and surface morphology—that significantly influence their catalytic and physical properties. PdNPs can adopt various morphologies such as spherical, cubic, rod-like, or octahedral forms, with each distinct shape affecting their reactivity and stability during catalytic processes. Typically ranging from 1 to 100 nm in size, smaller PdNPs often demonstrate superior catalytic activity due to their increased surface-area-to-volume ratio.[56] In addition, PdNPs can crystallize into different structures, most commonly face-centered cubic (FCC) or hexagonal close-packed (HCP) arrangements[57], which determine their atomic configuration and consequently influence their chemical behavior. [58] The surface structure of PdNPs is highly dynamic during catalytic cycles, often undergoing restructuring that can either enhance or diminish their catalytic performance. [59]

Moreover, PdNPs frequently exhibit surface defects such as vacancies, steps, and edges, which serve as active sites for catalytic reactions. [60] Due to these structural characteristics, PdNPs are sensitive to changes in temperature and pressure, which can lead to sintering or aggregation under harsh reaction conditions.[61] To counteract these effects, stabilizing agents or ligands are commonly employed to maintain the structural integrity of PdNPs by preventing agglomeration and enabling better control over their size and shape during synthesis. [62]

I.5.3.b Optoelectronic Properties of Palladium Nanoparticles

Palladium nanoparticles (PdNPs) display unique optoelectronic properties attributed to their nanoscale dimensions, which induce quantum effects and modify their electronic behavior compared to bulk palladium...[63] A prominent optical characteristic of PdNPs is their capacity for light absorption in the visible and ultraviolet spectral regions. This absorption is attributed to the phenomenon of surface plasmon resonance (SPR).[64]
The SPR in PdNPs is influenced by particle size, shape, and the surrounding medium, resulting in tunable optical responses that make them promising candidates for sensing and imaging applications.[65] PdNPs can also display enhanced electronic conductivity and catalytic activity, which is linked to their ability to efficiently transfer electrons at the nanoparticle surface .[66] The electronic band structure of PdNPs is significantly modified compared to bulk Pd, exhibiting narrower band gaps and altered electron density states, which can influence their reactivity and optical characteristics.[67] Additionally, the interaction of **PdNPs** with light can be leveraged for plasmonic applications. The resultant enhanced electric fields at the nanoparticle surface enable methodologies such as **s**urface-enhanced Raman spectroscopy **(SERS)** and plasmonic photothermal therapy.[68] PdNPs are also studied for their potential applications in optoelectronic devices like solar cells and light-emitting diodes (LEDs), where their electronic properties can improve device efficiency.[69] To improve their utility in various optoelectronic applications, recent studies have concentrated on deciphering how the structural, optical, and electronic characteristics **of PdNPs** interrelate.[70]

I.5.3.c Chemical and Catalytic Properties of Palladium Nanoparticles

Palladium nanoparticles (PdNPs) are renowned for their exceptional catalytic properties, making them highly efficient in a diverse range of chemical reactions, especially within organic synthesis. [71] Essential for catalysis in reactions such as hydrogenation, oxidation, and carbon-carbon coupling, a key chemical property of PdNPs is their ability to activate and adsorb reactants on their surface Exhibiting superb catalytic activity, PdNPs enable the efficient formation of carbon-carbon bonds in cross-coupling reactions like Suzuki, Heck, and Stille. [72] The distinctive electronic structure of PdNPs, characterized by a balanced distribution of d-band and s-band electron densities, is also crucial to their catalytic behavior. [73] This structure enables them to activate a variety of reactants, including hydrogen and small organic molecules. [74]

PdNPs demonstrate superior performance in reactions such as the selective hydrogenation of alkenes, selective oxidation, and even C-H bond activation, highlighting their versatility as catalysts.[75] Factors like particle size, shape, and support material profoundly impact the catalytic activity of PdNPs. Generally, smaller nanoparticles are more reactive, a result of their higher surface-to-volume ratio. [76] **PdNPs** are generally very stable and resist deactivation across many catalytic cycles, though sintering or aggregation can happen under extreme reaction conditions. [77] «It is also easy to modify PdNPs with ligands like phosphines or amines. This modification helps manage their reactivity, stability, and selectivity in catalytic applications."[78]

II.1 Mesoporous Materials

Mesoporous materials are of great interest to catalysis [79]-[80]. Mesoporous materials with regular geometries have been recently paid much attention owing to their great potentials in practical applications such as catalysis, adsorption, separation, sensing, medical usage, ecology, and nanotechnology [81]-[82]According to IUPAC classification, they are defined as porous materials with diameter in the size range of 0.2–2.0 nm. In 1990, Kuroda and coworkers first reported the preparation of mesoporous silica with uniform pore size distribution from the layered polysilicate kanemite (FSM-16, Folded Sheet Materials).

A significant breakthrough in the mesoporous materials research has come when Mobil scientists disclosed the M41S family of materials, which have large uniform pore structures, high specific surface areas and specific pore volumes, including hexagonal-MCM-41cubic-MCM-48 and lamellar-MCM-50[83]-[84].

II.1.1 Mesoporous silica materials (such as MCM-41)

Mesoporous silica materials, such as MCM-41, are characterized by their highly ordered pore structures and large surface areas. MCM-41 features uniform hexagonal arrays of mesopores with tunable pore sizes, typically ranging from 2 to 10 nanometers. These materials are widely used as supports in catalysis due to their excellent thermal stability and high surface area, which facilitate efficient dispersion of active sites. The unique pore architecture of MCM-41 enables enhanced mass transport and accessibility of reactants to catalytic centers. Consequently, mesoporous silica materials play a vital role in improving the performance of heterogeneous catalysts in various chemical reactions.[85]

II.1.2 SBA Materials (Santa Barbara Amorphous)

SBA materials, named after Santa Barbara Amorphous, are a family of mesoporous silica with highly ordered pore structures similar to MCM-41 but typically possess larger pore sizes and thicker pore walls. SBA-15 is the most studied member, featuring hexagonally arranged cylindrical pores with tunable diameters ranging from 5 to 30 nanometers. These materials offer excellent thermal and hydrothermal stability, making them ideal supports for catalytic applications under harsh conditions. The well-defined pore architecture of SBA materials enhances the diffusion of reactants and products, improving catalytic efficiency. Due to their versatility, SBA materials are widely employed in catalysis, adsorption, and drug delivery systems.[86]

II.1.3 Metal and Hybrid Metal Mesoporous Materials

Metal and hybrid metal mesoporous materials combine the high surface area and porosity of mesoporous supports with the unique properties of metals or metal oxides. These materials incorporate metal species either within the silica framework or as nanoparticles dispersed on the mesoporous matrix. The synergy between the metal components and the porous structure enhances catalytic activity, selectivity, and stability. Hybrid materials can also include organic-inorganic frameworks, broadening their functional versatility for applications such as catalysis, sensing, and energy storage. Their tunable composition and structure make metal and hybrid mesoporous materials highly attractive for advanced catalytic systems.[87]

II.1.4 MOFs mesoporous (Metal-Organic Frameworks)

Metal-Organic Frameworks (MOFs) are crystalline porous materials composed of metal ions or clusters coordinated to organic ligands, forming highly ordered three-dimensional structures. MOFs exhibit exceptionally high surface areas and tunable pore sizes, often in the mesoporous range, making them ideal for applications in catalysis, gas storage, and separation. Their modular design allows precise control over chemical functionality and pore environment, enabling tailored catalytic properties. [88] The hybrid organic-inorganic nature of MOFs provides versatility unmatched by traditional porous materials. As emerging mesoporous materials, [89] MOFs offer promising opportunities for developing highly efficient and selective catalysts.[90]

II.2 MCM 41 Materials

MCM-41, which stands for Mobil Composition of Matter No. 41, is a synthetic mesoporous silica material initially introduced by researchers at Mobil Oil Corporation in the early 1990s. his material is part of the M41S family of mesoporous molecular sieves, characterized by its highly ordered, one-dimensional hexagonal structure of cylindrical pores [91]. The distinctive structural feature, along with its remarkable properties, has made MCM-41 a versatile material with applications in various fields, including catalysis, adsorption, and drug delivery.[92]

At its core, MCM-41 is a silica-based material with a mesoporous structure, where the pore diameters range from 2 to 50 nanometers.[93] This pore size range falls between microporous materials (with pore sizes < 2 nm) and macroporous materials (with pore sizes > 50 nm). What distinguishes MCM-41 is the long-range order of its pore structure, which forms a regular hexagonal lattice that, when observed along the pore axis, resembles a honeycomb pattern.[94] This organized structure is essential for its beneficial properties.

One of the key characteristics of MCM-41 is its exceptionally high surface area, frequently surpassing 1000 m²/g. [95]. This vast internal surface area offers a large interface for interactions with guest molecules, making it highly efficient in catalytic processes by facilitating the high dispersion of active sites. Additionally, the ordered mesopore structure contributes to a significant pore volume, allowing for the storage of a considerable amount of guest species, which is beneficial for applications such as adsorption and drug delivery.[96].

The synthesis of MCM-41 generally employs a templating method that uses self-assembling surfactant molecules, typically quaternary ammonium salts like cetyltrimethylammonium bromide (CTAB).[97] These surfactant molecules form micelles in an aqueous solution, serving as templates around which a silica source, such as tetraethyl orthosilicate (TEOS), polymerizes. The surfactant is then removed through calcination or solvent extraction. Extraction leaves behind the ordered mesoporous silica framework[98]. Crucially, the pore size of the resulting MCM-41 can be modified by adjusting the chain length of the surfactant used in the synthesis, allowing for control over its textural properties.

Although the pore walls of MCM-41 are made of amorphous silica, setting it apart from crystalline materials like zeolites, its ordered structure offers a strong framework for a wide range of applications.[99] However, the amorphous nature may also result in lower hydrothermal stability compared to certain other porous materials.

In conclusion, MCM-41 is a mesoporous silica material characterized by its well-ordered hexagonal arrangement of uniform pores, high surface area, large pore volume, and adjustable pore size.[100] These key characteristics have made it a fundamental material in mesoporous science, fostering innovation and facilitating progress in various technological fields.

II.3 Synthesis Methods

II.3.1 Sol-Gel Method

The sol-gel method is a flexible wet-chemical process commonly used to synthesize inorganic materials, especially metal oxides, at comparatively low temperatures.[101] This process entails the transformation of a system from a liquid "sol" (a colloidal suspension) into a solid "gel" phase, resulting in the formation of a three-dimensional network.

The process usually starts with a molecular precursor, often a metal alkoxide (M(OR)n), which is dissolved in a solvent, typically an alcohol.[102]. These precursors undergo successive hydrolysis and condensation reactions, leading to the formation of an oxide network. Hydrolysis entails the reaction of the metal alkoxide with water, resulting in the substitution of alkoxy groups (-OR) with hydroxyl groups (-OH) and the production of alcohol.[103] This step is often catalyzed by acids or bases, which influence the rate and extent of the reaction.

The sol-gel method offers several advantages, including excellent control over the composition and homogeneity of the final product, the ability to synthesize materials with high purity, and the possibility of forming various shapes and forms, such as thin films, fibers, and nanoparticles.[104]

II.3.2 Microwave assisted technique

Using this method, we can form materials with specific, well-controlled geometries like nanorods, nanowires, nanotubes, and porous networks**.** **[105]**

Its applications span numerous sectors, including chemistry, materials science, and food processing**,** demonstrating the widespread adoption of this technology**.[106]** Microwave heating offers a notable advantage in chemical synthesis by reducing reaction times and improving yields over conventional heating techniques. **.[107]** The reason for this is that microwaves can directly engage with polar molecules and ions**,** which leads to quick and uniform heating**.[108]**

Thanks to rapid and volumetric energy transfer**,** this technique allows for much faster reaction rates compared to traditional thermal heating.[109]

For nanomaterial synthesis**,** microwave-assisted techniques offer distinct advantages, including better size control, improved crystallinity, and energy efficiency**.**[110]

The use of microwave irradiation in materials chemistry has enabled the synthesis of ceramics, metal oxides, polymers, and composites exhibiting superior properties**.[111]**

Considered a green chemistry approach**,** microwave-assisted synthesis offers benefits like reduced solvent consumption, quicker reactions, and decreased energy use**.[112]**

II.3.3 Chemical Etching Technique

In chemical etching**,** chemical solutions (etchants) selectively remove material from the surface of a solid, such as metals or semiconductors**,** making it a subtractive manufacturingprocess.[113]

This process works by selectively dissolving a material with a chemical reagent; typically, a protective layer (resist) is used to prevent etching in certain regions.[114]

Chemical etching is ectensively applied in fields like microfabrication and photolithography to establish detailed patterns in integrated circuits, microelectromechanical systems (MEMS), and printed circuit boards (**PCBs**).[115]

Wet chemical etching involves liquid-phase etchants such as acids or bases, and the rate of etching depends on factors like temperature, concentration, and material crystallography.[116]

The technique offers advantages such as low equipment cost and simplicity, but it may lack the precision and anisotropy by dry etching methods.[117]

Chemical etching is also used in materials characterization to reveal microstructural features such as grain boundaries and phases by selectively attacking different components of a material.[118]

II.3.4 Application of Chemical Etching in Mesoporous Materials

Chemical etching is widely used to create and modify mesoporous structures in materials like silica, silicon, and transition metal oxides, enabling control over pore size, shape, and surface area.[119]

Chemical etching**,** typically using HF-based solutions, is applied to mesoporous silicon to selectively dissolve the silicon and form a pore network with diameters of 2–50 nm**.**[**120**]

Chemical etching also plays a role in removing templating agents or sacrificial components (for instance, in soft or hard templating), thereby forming the mesoporous framework in materials like mesoporous carbon or metal oxides.[121]

To enhance the performance of mesoporous materials in applications such **as** catalysis, drug delivery, and adsorption**,** etching is applied post-synthesis to optimize pore connectivity and surface chemistry.[**122**]

For photocatalysis and energy storage applications**,** mesoporous TiO_2 or SiO_2 synthesis benefits from selective etching**,** which removes less stable framework regions to enhance mesoporosity and specific surface area[**123**].

II.4 Applications of Mesoporous Materials

These materials are extensively used in catalysis because their ordered pore structures facilitate efficient diffusion of reactants and stabilize active catalytic species.[124]

Because of their biocompatibility and high loading capacity**,** mesoporous silica nanoparticles **(MSNs)** are utilized in drug delivery systems **to** encapsulate and precisely release therapeutic molecules.[125]

With their large surface area and functionalisable pore walls, mesoporous materials are effective in adsorption and separation technologies for trapping heavy metals, dyes, and gases.[126]

In energy storage devices like lithium-ion batteries and supercapacitors**,** they are essential, as mesoporosity boosts ion transport and the electrode–electrolyte interface.[127]

Mesoporous TiO_2 and related oxides enhance light-harvesting and charge separation capabilities in photocatalysis**,** which improves the efficiency of both pollutant degradation and water splitting.**[128]**

Mesoporous materials are also employed in biosensors, where the high surface area facilitates effective immobilization of biomolecules, enhancing sensitivity and selectivity.[129]

II.4.1 Catalysis and the Support Role of Mesoporous Materials

A chemical process known as catalysis involves a catalyst that increases the rate of a chemical reaction, though the catalyst itself is not permanently consumed or altered.[130]

By offering an alternative, lower activation energy pathway, catalysts improve how efficiently reactions proceed[131].

Catalysts enhance reaction efficiency because they create a new reaction route with reduced activation energy.**[132]**

The high dispersion of active catalytic species made possible by these characteristics enhances both catalytic activity and selectivity.**[133]**

By allowing for functionalization**,** the tunable surface chemistry of mesoporous materials leads to better metal-support interactions and enhanced catalytic stability.

Plus, the open mesoporous channels make it easier for reactants and products to move, which is vital in heterogeneous catalysis.**[134]**

In the petrochemical, environmental, and fine chemical industries, mesoporous supp**orts** such as **SBA-15, MCM-41, and KIT-6** are widely employed for acid, base, and redox catalysis**.[135]**

II.5 Ceramic Method for Preparing Supported Catalysts on Mesoporous

II.5.1 ceramic Methods,

In the ceramic method **(**also known as the solid-state or high-temperature mixing method**),** metal precursors are physically mixed with support materials and then subjected to high-temperature calcination to produce a catalyst.[136]

It is a traditional method for manufacturing heterogeneous catalysts, particularly favored where thermal stability and the need **for** large-scale production are key.[137]

To prepare mesoporous materials using the ceramic method, a mesoporous support (e.g., **SBA-15 or MCM-41**) is generally mixed with a metal oxide precursor and then calcined at high temperatures (e.g., 500-900°c).[138]

Through calcination, metal precursors decompose and the active phase becomes integrated with the support matrix, yielding a thermally stable catalyst**.[139]**
Compared to wet impregnation or sol-gel techniques, the ceramic method can result in poorer metal particle dispersion**,** particularly in mesoporous supports with fragile structures.[140]

The ceramic method remains valuable for applications that require sturdy catalysts**,** including automotive exhaust treatment and high-temperature reforming reactions,despiteitslimitations.[141]

II.5.2 Soft Chemistry Methods for Preparing Supported Catalysts

Chimie douce**,** or the soft chemistry method**,** refers to synthesis techniques that use low temperatures and solutions to make solid-state materials, typically in mild or ambient environments[142].it is used in catalyst preparation to introduce metal species into mesoporous supports like **MCM-41, SBA-15, or KIT-6** through techniques such as sol-gel, ion exchange, or infiltration.[143]

The sol-gel process is a frequent soft chemistry route; it involves the hydrolysis and condensation of metal precursors within a templated mesoporous matrix, which guarantees homogeneous dispersion of catalytic sites.[144]
Precise control of composition, porosity, and metal-support interactions is achieved with this

method, making it crucial for catalytic performance in areas such as oxidation, hydrogenation, and photocatalysis.With soft this techniques, we can also synthesize hybrid or multifunctional catalysts, adding organic or bioactive groups to mesoporous frameworks alongside metal species.[145]

Soft chemistry methods are seen as green and scalable due to their low energy needs and high versatility, which makes them ideal for both laboratory and industrial catalyst preparation.[146]

II.5.2.a Sol-Gel Method

The sol-gel method is a chemical process that begins with the hydrolysis and condensation of metal alkoxides or inorganic salts to form a sol, which then develops into a gel-like network.**[147]**

We can precisely and uniformly integrate active catalytic components, such as metal oxides or nanoparticles, into or onto a support matrix using this technique.[148]

Utilizing the sol-gel method in supported catalyst preparation enables the placement of catalytic species onto high-surface-area substrates, including silica, alumina, and mesoporousmaterials.[149]

Drying and calcination follow gelation. This process eliminates solvents and organic matter, converting the precursor into the active catalytic phase.

Catalysts made via the sol-gel process show enhanced performance, a benefit stemming from the method's ability to achieve excellent metal dispersion, promote strong metal-support bonding, and design specific pore structures.[150]

This method is extensively used in catalyst fabrication for processes such as oxidation, reduction, photocatalysis, and environmental remediation, owing to its simplicity, scalability, and versatility.[151]

II.5.2.b Co-Precipitation Method:

This technique involves the simultaneous introduction of metal precursors and a precipitating agent (e.g., NaOH or NH_4OH) into a solution containing a mesoporous support (e.g., SBA-15 or MCM-41). The mesoporous structure subsequently serves as a confinement matrix, facilitating the integration of metal hydroxides or oxides within its pores.[152]

Once aged, the material is filtered, washed, and then subjected to drying and calcination. These steps are crucial for converting the metal precursors into their catalytically active oxideform.**[153]**

This technique promotes high metal dispersion, inhibits agglomeration, and improves the interface between the active phase and the mesoporous support.[154]

Crucially, the mesoporous materials largely retain their pore structure and surface area, thereby preserving their favorable textural properties.[155]

II.5.2.C.Impregnation method:

The impregnation method is a common technique used to deposit active components (like metal ions or nanoparticles) onto a solid support.It typically involves contacting the support material with a solution of the precursor of the active species, allowing it to adsorb or fill the pores of the support.There are two main types of impregnation: incipient wetness (dry) impregnation and wet impregnation[156] :

In incipient wetness impregnation, the volume of the precursor solution is just sufficient to fill the pore volume of the support, ensuring uniform distribution without excess liquid.[157]

In wet impregnation, excess solution is used, and the support is soaked in the precursor solution for a certain time, followed by drying and calcination.[158]

After impregnation, drying is necessary to remove the solvent and promote precursor-support interaction.[159]

Calcination is often performed after drying to decompose the precursor and form the active catalytic phase.The distribution and dispersion of the active component depend on factors like support pore structure, solution concentration, and drying conditions.[160]

II.6.rameters influenciing catalytic propreties :

1. **Surface Area of the Catalyst:**
   A higher surface area increases the number of active sites available for reaction, enhancing catalytic performance.[161]
2. **Pore Structure (Size and Volume):**
   The accessibility of reactants to active sites depends on the pore size distribution; mesoporous materials often offer better diffusion characteristics.[162]
3. **Particle Size of the Active Component:**
   Smaller metal particles often exhibit higher dispersion and more unsaturated surface atoms, which enhance catalytic activity.[163]
4. **Electronic Properties and Oxidation States of Active**

5. **Sites:**

   The electronic configuration and oxidation state of metal centers determine their ability to adsorb and activate reactants.[164]

6. **Metal-Support Interaction:**

   Strong interactions between metal particles and supports can influence dispersion, stability, and electron transfer, affecting activity and selectivity.[165]

7. **Acid–Base Properties of the Catalyst Surface:**

   Acidic or basic sites can influence reaction pathways, especially in acid/base-catalyzed processes (e.g., cracking, isomerization).[166]

8. **Thermal Stability:**

   A catalyst must maintain its structure and activity under high-temperature conditions commonly encountered in industrial processes.[167].

9. **Redox Properties:**

   Catalysts that can reversibly undergo oxidation/reduction (e.g., CeO_2, MnO_x) are critical in reactions involving oxygen transfer.[168]

10. **Preparation Method and Conditions:**

    Synthesis routes (e.g., impregnation, co-precipitation) affect catalyst texture, dispersion, and homogeneity, thus influencing performance.[169]

III.1.General information of lawsonia inermis :

Lawsonia inermis L., universally known as **henna**, is a fascinating plant whose history and uses are intertwined with numerous cultures across the globe. Henna is a shrub or small tree belonging to the Lythraceae family. It typically grows 2 to 6 meters tall, but can sometimes reach up to 12 meters. It's characterized by its extensive branching, smooth (glabrous) appearance, and the potential presence of thorny twigs, especially on older plants.[170]

FigureI.4 :Lawsonia inermis

III.1.1 Botanical Identification of Henna [171] :

Family : **Lythraceae**

Nom scientifique (genre) : lawsonia inermis

III.1.2 Common Botanical Characters :

Table I.5 [172] **:** the information about Lawsonia inermis morphology

Feature	Description
Bark	Greyish-brown, smooth or striated.
Twigs	Young branches are quadrangular and green, turning reddish with age.
Leaves	Opposite, entire, subsessile, elliptic to broadly lanceolate in shape. They typically measure 1.5 to 5 cm long and 0.5 to 2 cm wide, are glabrous, with an acuminate apex (tapering to a point) and slightly depressed veins on the upper surface.
Flowers	Small, numerous, very fragrant, white to cream or sometimes reddish in color. They are arranged in large, pyramidal terminal cymes. Each flower has four crumpled petals in the bud and eight stamens inserted in pairs.
Fruits	Small, globose (spherical) brown capsules, 4 to 8 mm in diameter, containing numerous seeds. They open irregularly into four sections.
Seeds	Approximately 3 mm wide, angular, with a thick, brown seed coat.

V.Conclusion :

In essence, the biosynthesis of palladium nanoparticles and MCM-41 composites using plant extracts is poised to revolutionize water purification technologies. This approach aligns perfectly with global sustainable development goals by offering environmentally benign, highly efficient, and economically viable solutions for addressing critical water quality challenges. Continued research into understanding the precise mechanisms of plant-mediated synthesis and optimizing the properties of these advanced nanomaterials will undoubtedly unlock their full potential, paving the way for truly sustainable and next-generation water remediation strategie**..**

CHAPTER II MATERIALS AND METHODS

I. Introduction:

The first part is devoted to the preparation of the extract from **lawsonia Inermis** leaves, followed by the synthesis of the nanocomposite **Pd-MCM41.**

The second part focuses on the study of the photodegradation of methylene blue using the **Pd-MCM41** nanocomposite.

II. Chemicals Used:

Table II.*1*: List of Chemicals Used

Produit	Symbole
Palladium(II) Chloride	PdCl2
Mobil composition of matter No41	MCM41

***Lawsonia Inermis*:** Fresh and healthy leaves were collected from nearby farms in Tlemcen (Ouest of Algeria) on **22/02/2025** After properly cleaning them with flowing tap water to get rid of any dirts or other polluted organic materials, they were repeatedly rinsed in de-mineralized water. The fresh leaves were crushed.

Pollutants Used:

Methylene bleu: It is a dye that belongs to the family of cationic dyes. Its molecular formula is $C_{16}H_{18}N_3ClS$, and its molar mass is **319.85 g/mol**."

III. Preparation method for the extract of lawsonia Inermis leaves:

In an Erlenmeyer flask, we put 1 g fresh leaf of lawsonia Inermis and we add 100 mL of distilled water; the mixture is heated on a magnetic stirrer hot plate with simultaneous stirring at 80°c for 30minutes.
It is allowed to cool, then filtered, and stored in the refrigerator.

VI.Biosynthesis of Pd-MCMC41 nanocomposite:

In a beaker, 0.017 mg of $PdCl_2$ is added to 100 mL of distilled water along with 2 mg of NaCl, and the mixture is placed on a stirring hot plate for one hour. The mixture is stirred until complete dissolution. We add to it 25 ml of previously prepared leaf and let them continuously stirred for 24 hours.

Following incubation, the mixture is centrifuged at 5000 t/m and subsequently dried in an oven at 50°C for 24 hours. A grey material is obtained.

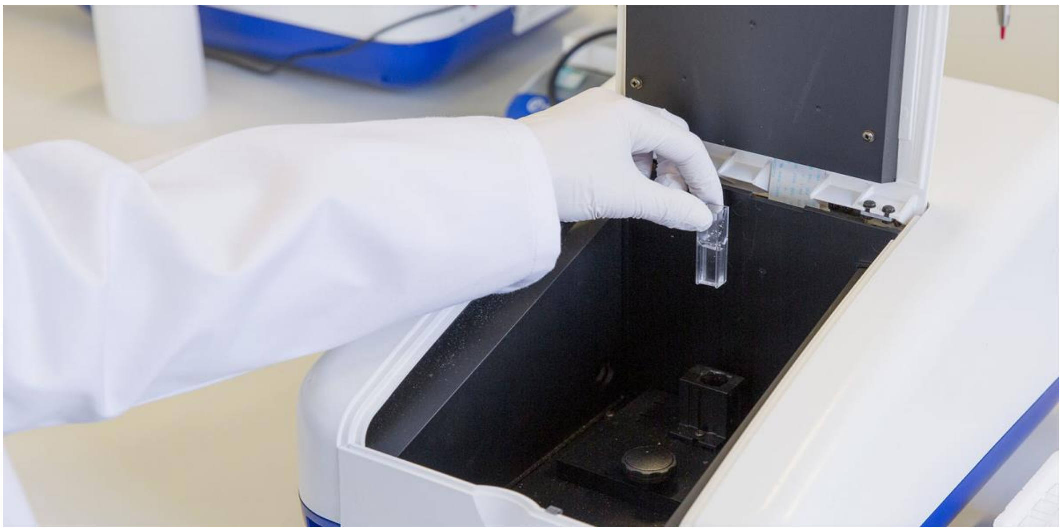
V.Les techniques de caracterisation :

V.1.UV visible Spetroscopy :

V.1.a.Definition:

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light absorbed or transmitted through a sample, relative to a reference or blank sample. Based on the absorption of high energy **(λ= 200 - 800 nm)"** (Direct and literal). This property is influenced by the sample's composition, potentially providing information about what is in the sample and at what concentration. Since this spectroscopic technique relies on the use of light, let's first consider the properties of light.

This technique offers both qualitative insights into the nature of bonds within a sample and quantitative determination of the concentration of species that absorb in this spectral range. This non-destructive and rapid technique is widely used in practical chemistry, as well as in chemical and biochemical analysis. [173]



FigureII.1 : **Image of an ultraviolet spectrophotometer**[174]

V.1.b. Principles of UV visible :

When ultraviolet and visible radiation strikes a surface, it can interact with matter in several ways:

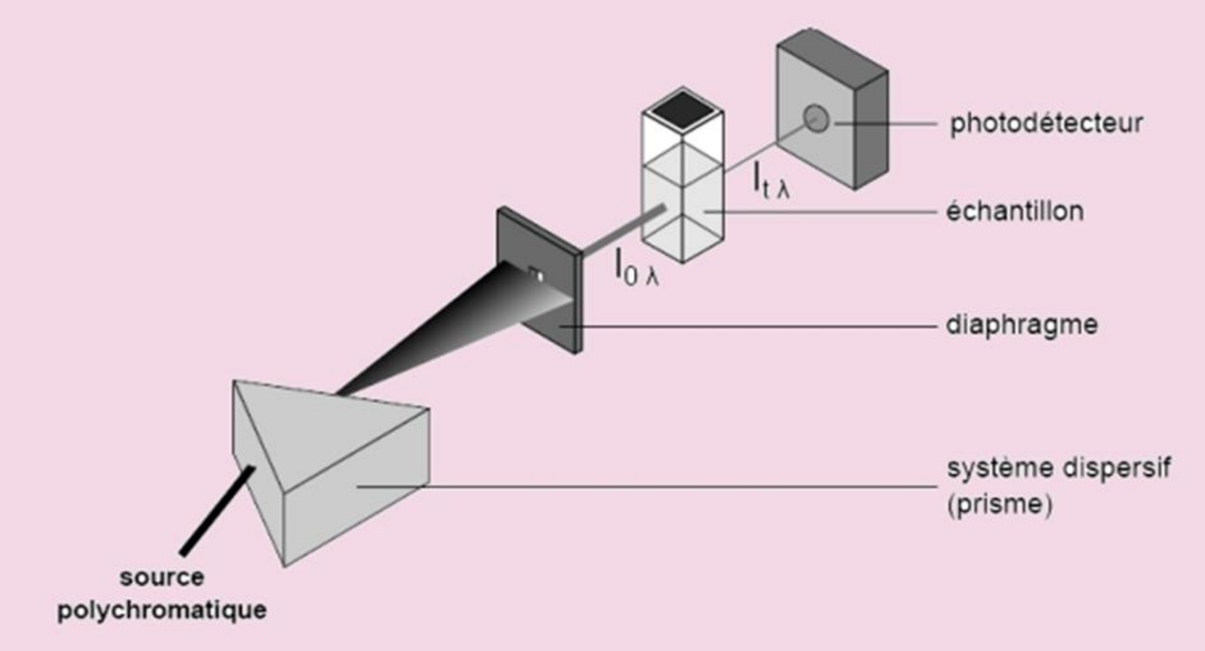
- It can be transmitted, either directly or in a diffuse manner.
- It can be reflected, which can occur either specularly (like a mirror) or diffusely (scattered in many directions).
- It can be absorbed.

- It can be absorbed and then emitted as photoluminescence (either fluorescence or phosphorescence).
- Finally, it can be laterally diffused at wavelengths different from the incident monochromatic radiation, a phenomenon known as Raman scattering (or the Raman effect[175].

A polychromatic light source (emitting in the UV or visible range) is placed before a prism. This dispersive system breaks down the polychromatic radiation from the source. By correctly positioning a diaphragm-sample-photodetector system, the solution in the cuvette will be irradiated with nearly monochromatic light.

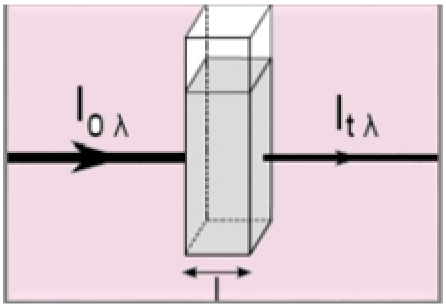
The diaphragm, a simple narrow slit, ensures the sample is illuminated with a beam of minimal width, thereby providing high-quality monochromatic light. The photodetector then measures the intensity of the light transmitted through the sample solution, denoted as it, λ.

Practically, the sample consists of the compound being studied, dissolved in a solvent, and held within a cuvette. It is crucial that neither the solvent nor the cuvette interferes with the measured data [176].



FigureII.2: Schematic principle of an ultraviolet spectrometer

177



FigureII.3: Scheme illustrating the intensity of transmitted and absorbed radiation

Understanding the Beer-Lambert Law

The Beer-Lambert Law, formulated by Lambert and Beer, describes how the intensity of light absorption correlates with the concentration and path length of an absorbing species. This law, often referred to as Beer's Law, is strictly valid for absorbing materials within dilute, homogeneous solutions: [178]

$A=\epsilon bc=-\log T=\log(1/T)$

Here's what each symbol means:

- **A**: Absorbance
- **ϵ**: Molar absorptivity (or molar absorption coefficient)
- **b**: Thickness of the sample
- **c**: Concentration
- **T**: Transmittance

V.2.X-ray Diffraction (XRD) :

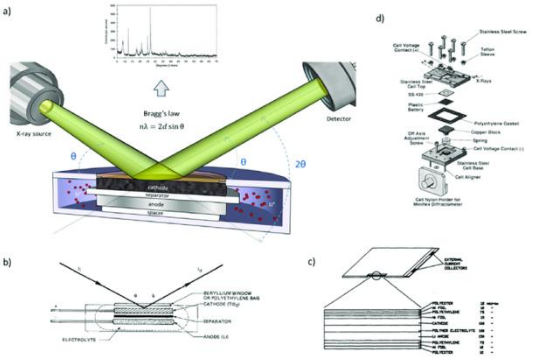
V.2.a.Definition :

XRD is a strong, non-destructive analytical method used to uncover the internal crystal arrangement of materials. It works by exploiting the constructive interference that occurs when monochromatic X-rays interact with the orderly atomic structure of a crystalline sample[179].

FigureII.4: X-ray diffraction image[180]

V.2.b.Principle of XRD:

The process works by firing X-rays at a material. When these X-rays hit the matter, they're scattered in every direction. What's special is that these scattered waves all share the same phase and wavelength. This scattering creates interference as the waves interact with the material's atomic planes. The result is a diffracted wave whose unique characteristics are directly linked to the material's internal crystalline structure [181].

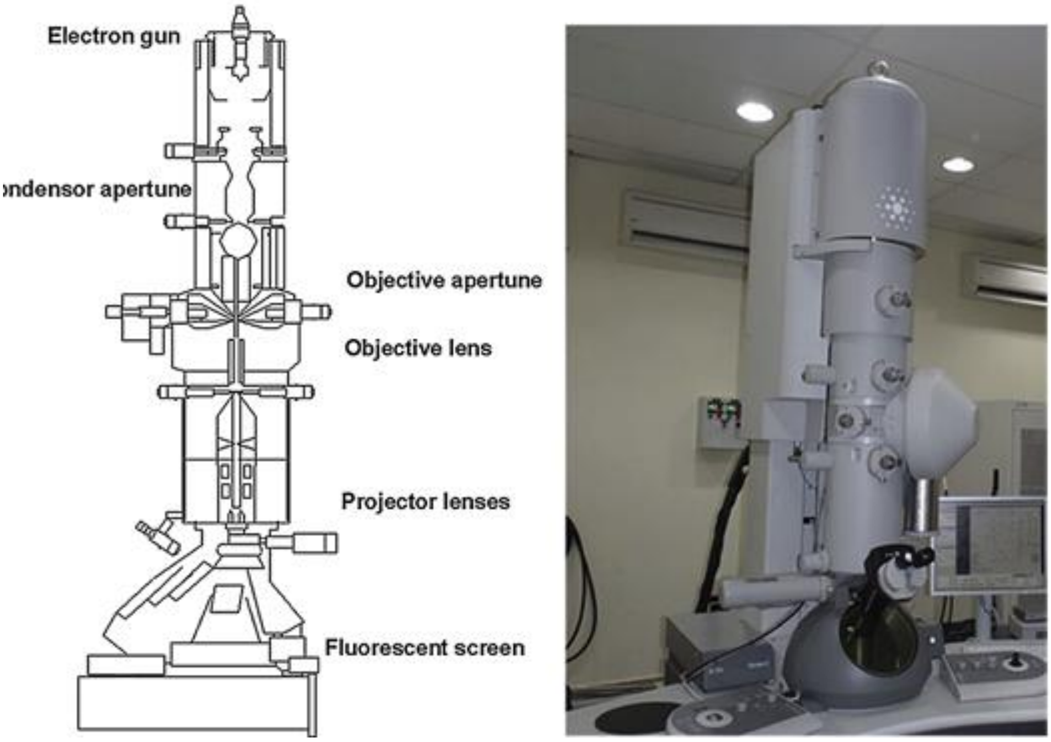


FigureII.5: Schematic principle OF X-ray diffraction

V.3.Transmission Electron Microscopy (TEM):

V.3.a.definition:

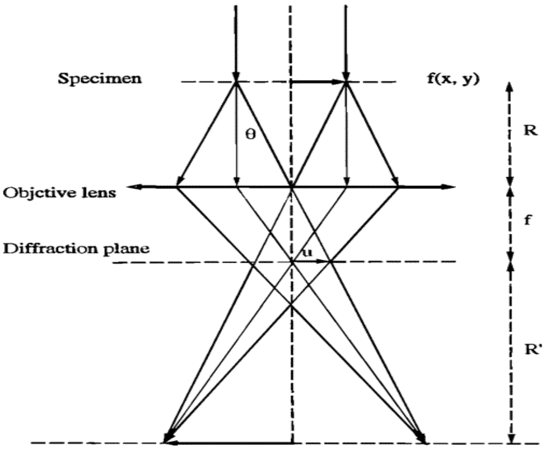
Transmission Electron Microscopy (TEM) is a potent and versatile analytical technique. It employs an electron beam to provide atomic-level insights into the internal structure, morphology, crystal structure, and composition of incredibly thin specimens.[182]



FigureII.6: schematic diagram of transmission electron microscope [183]

V.3.b.Principle:

The fundamental principle of **TEM** involves using an **electron beam** (instead of light) to pass through an extremely thin sample (typically under 100 nm thick). Because electrons have a significantly shorter **de Broglie wavelength** compared to visible light photons, TEM can achieve much higher resolutions than optical microscopes[184].

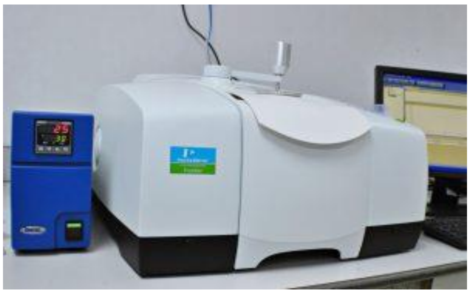


FigureII.7: principle of TEM[185]

V.4. Fourier-transform infrared FTIR:

V.4.a.Definition:

Fourier Transform Infrared (FTIR) spectroscopy is a powerful analytical technique that generates a material's infrared absorption or emission spectrum, effectively creating a unique "molecular fingerprint[186].



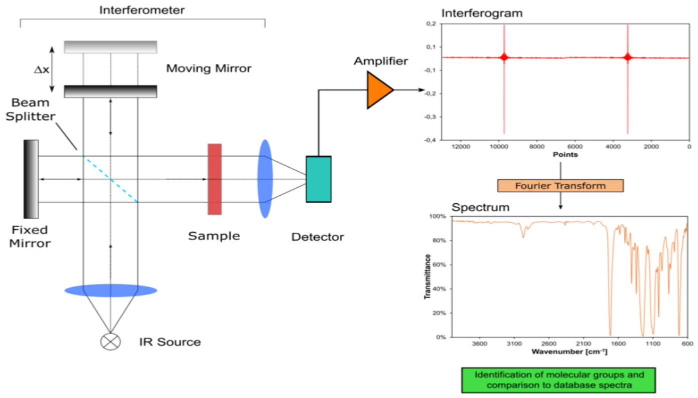
FigureII.8: Image of FTIR

V.4.b.Principle:

Functional groups were identified using Fourier-transform infrared (FT-IR) spectral analysis on a Perkin Elmer spectrophotometer, covering the 500 to 4000 cm^{-1} range.

The surface morphology of the prepared samples was examined with an Emcraft (Seoul, South Korea) cube compact model scanning electron microscope (SEM). This instrument also provided elemental analysis and sample purity through energy dispersive spectroscopy (EDS).

UV-Vis absorbance spectra for the nanocomposites were collected on a Tensor II BRUKER (Massachusetts, USA) UV-Vis spectrophotometer. These spectra were recorded at room temperature in air, spanning wavelengths from 200 to 800 nm.
Additionally, a professional double-beam UV/Vis spectrophotometer (C-7200S) was used to analyze dye concentration[187].



FigureII.9:Schematic principle of FTIR

VI.Study of parameters influencing the formation of nanoparticles:

VI.1.Preparation of solutions:

TableII.2.Different ratios of extract to PdCl2 solution were studied in 6 tubes

1. Tube Number	Extract : $PdCl_2$ Solution Ratio	Volume Ratio (Extract : $PdCl_2$ Solution)
1	1:9	1 part Extract : 9 parts $PdCl_2$ Solution
2	2:8	2 parts Extract : 8 parts $PdCl_2$ Solution
3	3:7	3 parts Extract : 7 parts $PdCl_2$ Solution
4	4:6	4 parts Extract : 6 parts $PdCl_2$ Solution
5	5:5	5 parts Extract : 5 parts $PdCl_2$ Solution
6	6:4	6 parts Extract : 4 parts $PdCl_2$ Solution

After determining the maximum production of nanoparticles, we then study the parameters that influence their production, which are:

VI.1.a. Different PH:

1mL of our extract is mixed with 9 mL of PdCL2 at five different pH levels: 3,5,7, 9, and 11. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust the pH. The synthesis of NPs was confirmed by UV-Visible spectrophotometric analysis. [188]

VI.1.b. Different T°:

In a tube, 1 mL of our extract is combined with 9 mL of PdCL2. This mixture is then placed in a water bath, and the temperature is set at 30°C, 40°C, 50°C, and 60°C for different trials.The synthesis of NPs was confirmed by UV-visible. [189]

VI.1c. Different time:

First, to optimize the incubation time, reactions were conducted for four different durations: 0h, 30min,1h ,3h and 24h. We kept the volume of our extract at 1 mL and the PdCL2 at 9 mL to form the stock solution. After each period, all reactions were monitored using a UV-visible spectrophotometer.

VI.1.d. Different concentrations:

To study the effect of our extract's concentration on NPs synthesis, various concentrations (10−3,3×10−3, 5×10−3, and 8×10−3) were used while keeping the other two parameters fixed. During the synthesis, 1 mL of each concentration and9 mL of PdCL2 were mixed. NPs synthesis was confirmed by UV-Visible spectrometric analysis. **[190]**

VII.Study of degradation test of methylene bleu:

A methylene bleu solution with a concentration of $5\times10-5$ M was prepared by mixing an appropriate amount of BM with distilled water.

This study investigates the degradation of methylene blue (MB) in distilled water by measuring its absorbance using a UV spectrophotometer over a total duration of 150 minutes, with readings taken every 15 minutes. Three distinct experimental conditions are tested under a 75-watt lamp: first, the MB solution alone serves as a control to assess the lamp's inherent intensity effect; second, the degradation is observed with the addition of a small amount of MCM-41 to the MB solution; and finally, the process is evaluated with the incorporation of 1 mg of Pd-MCM-41 into the MB solution, aiming to determine the enhanced photocatalytic efficiency of the composite material [191].

VII.1.Study of some parameters influencing the photodegradation of MB:

We add 1mg of Pd-MCM41 to our BM solution.

VII.1.a. Effect of Pd-MCM41 quantity:

We add 1 mg of our Pd-MCM-41 nanocomposite to the methylene blue solution already in a cuvette, set the pH to neutral, and then place it in front of a 75-watt lamp for 15 minutes before measuring the absorbance for a total of 150min.

The same operation is repeated with 2 mg and 3 mg of Pd-MCM-41.

VII.1.b. Effect of methylene bleu concentrations:

We studied the photodegradation of methylene blue (MB) using various initial MB concentrations: $10-5$;$3.10-5$ and $5.10-5$ with each experiment conducted over a 150-minute period. [192]

VII.1.c. Effect of lamp intensity:

You are studying the effect of lamp intensity on the photodegradation of methylene blue (MB) ; using various lamp intensities :75 watt ;100 watt and 200 watt and observing the degradation over different periods. [193]

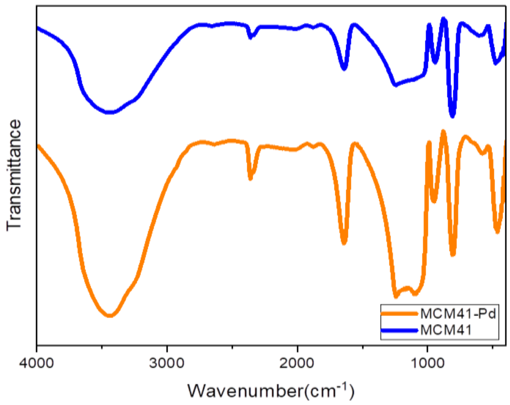
CHAPTER III: RESULTS AND DISCUSSIONS

I.Introduction::

Water pollution, fueled by industrialization and population growth, poses a significant threat to both environmental and public health. Among the many pollutants, synthetic dyes, discharged from industries such as textiles and pharmaceuticals, are particularly concerning due to their high visibility, toxicity, and resistance to conventional treatment methods[194]-[195].

II.FTIR :

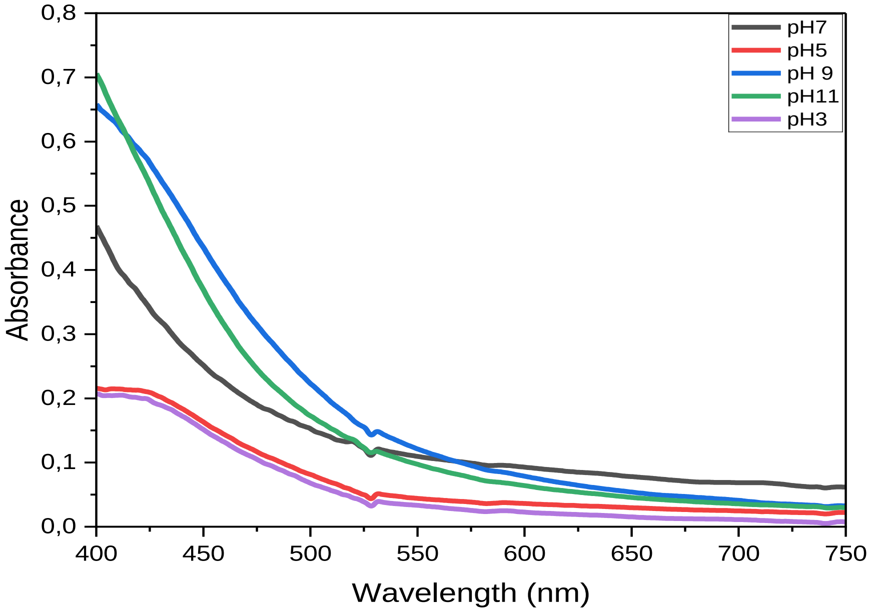
The FTIR spectra of MCM-41 Pd en Bleu and MCM-41 en Orange reveal distinct functional groups and characteristics. Both materials exhibit a Si-O-Si stretch around 1100 cm^{-1}, representing the silica network, and a Si-OH stretch near 950 cm^{-1}, indicative of surface hydroxyl groups. However, the MCM-41 Pd en Bleu spectrum is distinguished by a Pd-O stretch between 600–700 cm^{-1}, suggesting the presence of palladium within the silica matrix, which is absent in MCM-41 en Orange. Additionally, both materials may show C-H stretching bands around 2850–2950 cm^{-1} if organic modifications are present. The color change from blue to orange could be attributed to different metal incorporations or surface functionalization, which might alter the position or intensity of certain bands, particularly in the 500–800 cm^{-1} range. In conclusion, while the basic structural features of both materials are similar, the incorporation of palladium in MCM-41 Pd en Bleu introduces unique spectral features, making it distinct from MCM-41 en Orange, where such metal-specific bands are not observed..



**FigureIII.1 : FTIR of MCM41 (i)
and Pd-MCM41 (ii)**

III.Study of parameters influencing the formation of nanoparticles :

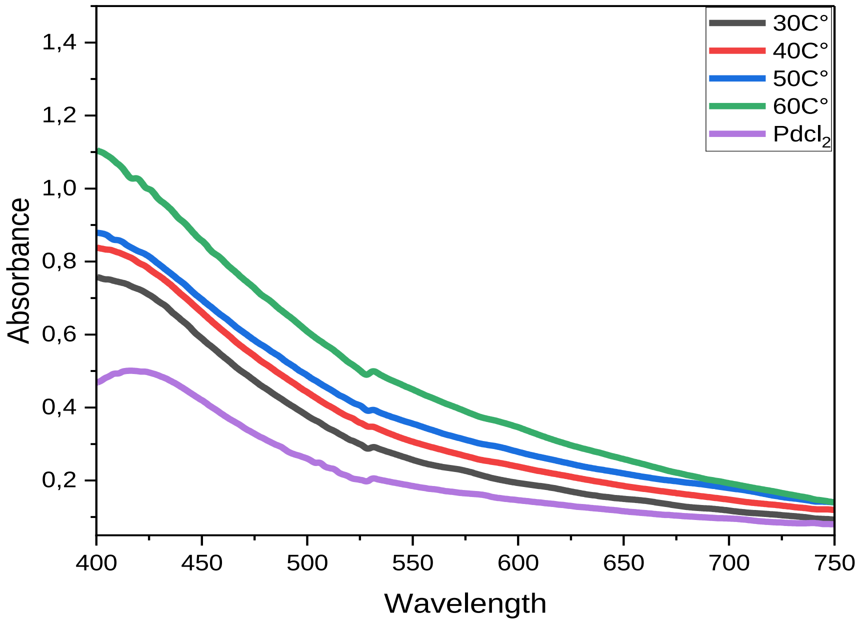
-The study investigating the influence of varying pH values(3, 5, 7, 9, and 11) on the formation of palladium nanoparticles (PdNPs) revealed a notable trend. Absorbance measurements indicate an increase in PdNP formation as the pH shifts from acidic towards alkaline conditions. This observation highlights the critical role of pH as a controlling parameter in the synthesis of palladium nanoparticles, influencing their nucleation and growth in the aqueous medium. Further detailed analysis of size, morphology, and stability at these different pH values would provide a more comprehensive understanding of this effect [196].



FugureIII.2 : :UV-Vis Absorbance Spectra of Palladium Chloride ($PdCl_2$) Solutions at Various PH

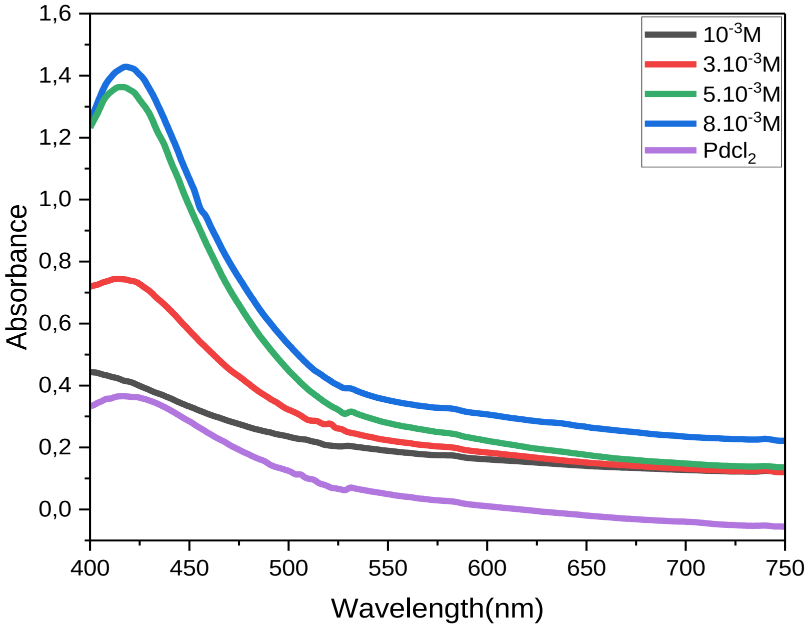
-temperature stands out as a critical parameter, profoundly influencing the size, morphology, and crystallinity of Pd-NPs. Reliable palladium nanoparticle syntheses in aqueous solution: the importance of understanding precursor chemistry and growth mechanism. [197] Our study systematically investigated the influence of synthesis temperature (30°C, 40°C, 50°C, and 60°C) on palladium nanoparticle (Pd NP) formation. We observed that lower temperatures (30°C and 40°C) typically promoted more controlled nucleation and growth, leading to smaller, more uniform Pd NPs with narrower size distributions Synthesis methods and applications of palladium nanoparticles: A review. [198] As the temperature increased to 50°C and 60°C, the reaction kinetics accelerated considerably

.



FigureIII.3:UV-Vis Absorbance Spectra of Palladium Chloride ($PdCl_2$) Solutions at Various T°

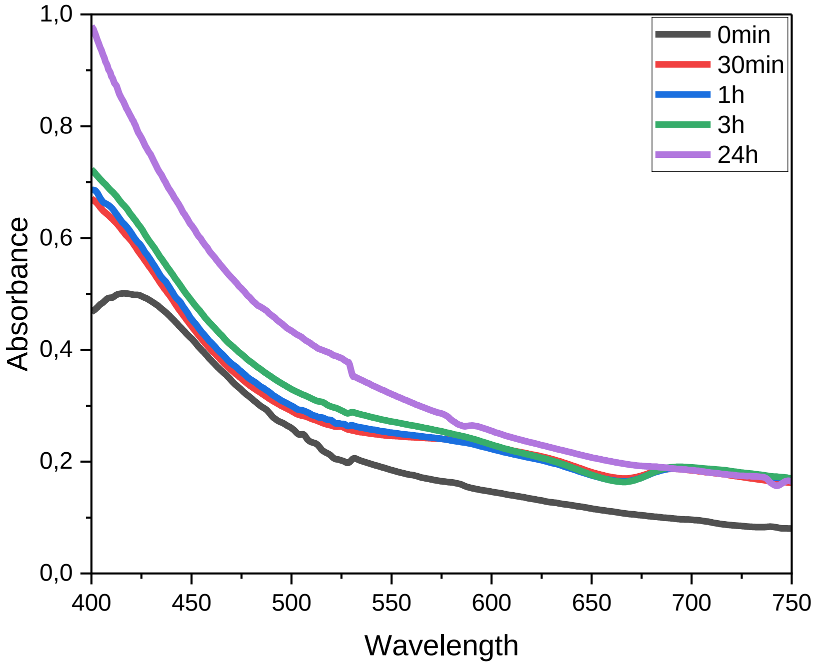
-This study explores also the time-dependent synthesis of palladium nanoparticles (PdNPs) by tracking variations in their optical absorbance using UV-Visible spectroscopy at specific time intervals: 0 min, 30 min, 1 h, 3 h, and 24 h. At the initial time point (0 min), the precursor solution exhibited no distinct absorbance features associated with metallic palladium, indicating that nanoparticle formation had not yet commenced. After 30 minutes, a gradual increase in absorbance intensity was detected, marking the onset of nucleation and the initial formation of Pd nanoparticles. By 1 hour, the absorbance became more pronounced, indicating continued particle growth and an increase in nanoparticle concentration. This upward trend persisted up to 3 hours, at which point the absorbance began to stabilize, suggesting a transition from rapid growth to a more stable phase. After 24 hours, the absorbance remained relatively unchanged, implying that the nanoparticle formation had reached a steady state. Overall, this study demonstrates a time-dependent increase in PdNP formation, as evidenced by the progressive changes in optical absorbance [199]



FigureIII.4: UV-Vis Absorbance Spectra of Palladium Chloride ($PdCl_2$) Solutions at Various Concentrations

The influence of the extract concentration on the synthesis of palladium nanoparticles (PdNPs) was investigated by varying the concentration of the extract while maintaining all other parameters constant. Four different concentrations (1×10^{-5}, 3×10^{-3}, 5×10^{-3}, and 8×10^{-3} mM) were tested. For each experiment, 1 mL of the extract solution was mixed with 9 mL of a fixed $PdCl_2$ solution, and the formation of PdNPs was monitored using UV-Visible spectroscopy.

At lower extract concentrations (1×10^{-5} mM), the UV-Visible absorbance spectra displayed a weak and broad peak, indicating limited reduction of Pd^{2+} ions and the formation of fewer or smaller nanoparticles. As the extract concentration increased to 5×10^{-3} and 8×10^{-3} mM, the absorbance intensity significantly increased, and a sharper, well-defined surface plasmon resonance (SPR) peak emerged. This shift suggests more efficient nucleation and growth of palladium nanoparticles due to the greater availability of reducing and stabilizing agents in the extract [200]

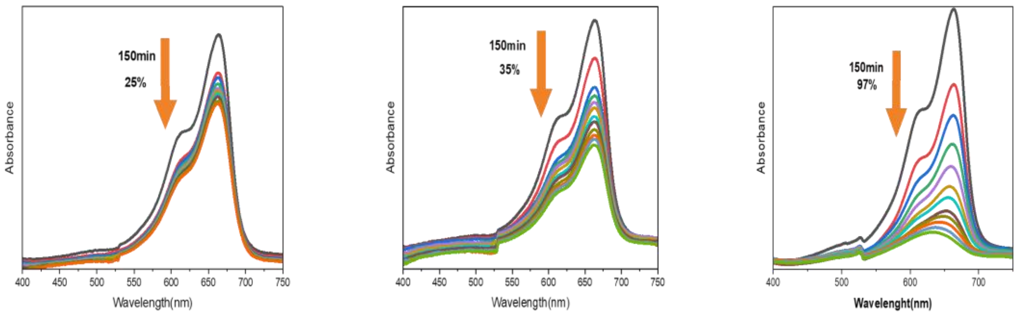


FigureIII.5 : UV-Vis Absorbance Spectra of Methylene Blue Solution During Degradation Over Time

IV.Study of degradation test of MB :

The photocatalytic degradation of methylene blue (MB) under visible light was examined under three different conditions: (a) irradiation with a 75-watt lamp in the absence of any catalyst, (b) in the presence of pure MCM-41, and (c) using palladium-supported MCM-41 (Pd/MCM-41) as the photocatalyst.In the absence of any catalyst (exposure to light alone), only a slight reduction in absorbance was recorded, indicating limited photodegradation of methylene blue under visible light. The addition of MCM-41 led to a moderate improvement in degradation efficiency, likely due to its high surface area, which promotes dye adsorption and contributes marginally to catalytic activity.A significantly enhanced degradation effect was observed when Pd/MCM-41 was used. A sharp decline in absorbance occurred within the first 60 minutes, followed by continued degradation, resulting in near-complete decolorization of the dye solution after 150 minutes. This superior performance can be attributed to the synergistic interaction between palladium nanoparticles and the mesoporous MCM-41 matrix. Palladium facilitates charge carrier separation and promotes the generation of reactive oxidative species, while MCM-41 serves as a high-surface-area platform for efficient light absorption and dye adsorption.

Overall, the findings clearly indicate that Pd/MCM-41 outperforms both MCM-41 and light-only conditions, highlighting its potential as an effective photocatalyst for visible-light-driven degradation of organic pollutants.[201]



(a) **(b)** **(c)**

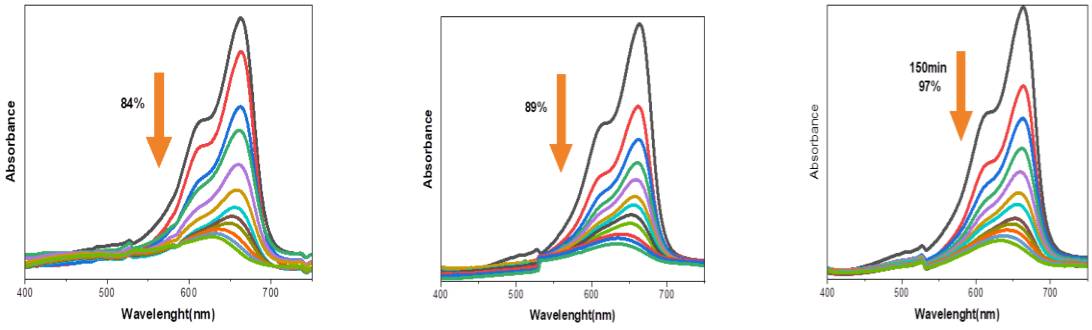
FigureIII.6:photodegradation of methylene blue by lamp intensity(a),MCM41(b) and Pd-MCM41(c)

IV.1.Study of some parameters influencing the photodegradation of MB :

IV.1.a.effect of Pd-MCM41 quantity :

The effect of the amount of Pd-MCM-41 catalyst on the photocatalytic degradation of methylene blue (MB) was investigated by varying the mass of Pd-MCM-41 added to the solution: 1 mg(a), 2 mg(b), and 3 mg(c). The experiments were conducted at neutral pH under irradiation from a 75 W lamp for 150 minutes, with absorbance measurements taken every 15 minutes.The results show a progressive degradation of methylene blue over time, with a significant improvement in the rate of decolorization as the amount of Pd-MCM-41 increases. Specifically, the decrease in the maximum absorbance at 664 nm, characteristic of MB, is faster and more pronounced with 3 mg of catalyst compared to 1 mg or 2 mg (figure).This enhancement can be attributed to the increased number of active Pd sites, which promote the generation of reactive species such as hydroxyl radicals (•OH) under UV-visible irradiation, thereby improving the efficiency of the photocatalytic degradation process [202]

La structure mésoporeuse de MCM-41 confère une grande surface spécifique permettant une meilleure dispersion des nanoparticules de Pd et une adsorption efficace des molécules de MB à proximité des sites actifs [203]

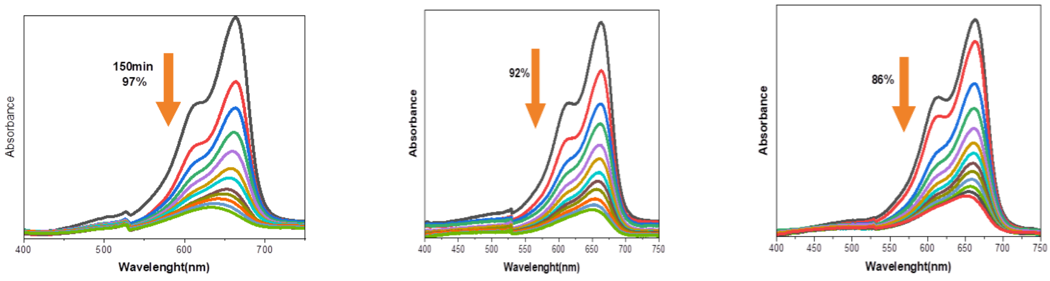


(a) **(b)** **(c)**

FigureIII.7: Effect of Pd-MCM41 quantity for the photodegrdaion of MB,1mg(a),2mg(b) and 3mg(c).

IV.1.b.Effect of methylene bleu concentration:

The effect of initial methylene blue (MB) concentration on its photocatalytic degradation under UV-visible light was examined at concentrations of 1×10^{-5} M(a), 3×10^{-5} M(b), and 5×10^{-5} M(c). All experiments were conducted over 150 minutes under identical conditions, including catalyst dosage (Pd-MCM-41), pH, and light intensity. The degradation process was monitored via UV-Vis spectroscopy by tracking the absorbance at 664 nm, the characteristic peak of MB.The results demonstrate that photocatalytic efficiency decreases with increasing initial MB concentration. At 1×10^{-5} M, a marked decline in absorbance was observed, indicating higher degradation efficiency. In contrast, at 5×10^{-5} M, the degradation was significantly slower and incomplete within the same timeframe. This inverse relationship between dye concentration and degradation efficiency aligns with previous findings, which suggest that lower concentrations enhance photon penetration and catalyst surface activation, thereby promoting the generation of reactive oxidative species such as hydroxyl radicals (•OH) [204].



(a) **(b)** **(c)**

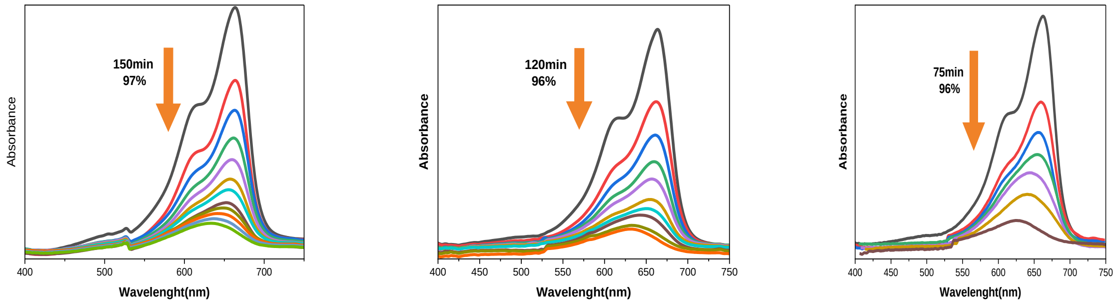
FigureIII.8: Effect of methylene bleu concentration for photodegradation of MB ,10 -

5 M(a),5*10 -5 M(b) and 8*10 -5 M(c)

IV.1.c.Effect of lamp intensity:

The photodegradation of methylene blue (MB) was investigated under varying lamp intensities: 75 W (a), 100 W(b), and 200 W(c).The findings indicate that the degradation rate of methylene blue (MB) is positively correlated with lamp intensity. At 75 W, the degradation proceeded slowly, marked by a minimal reduction in absorbance over time. With 100 W illumination, a moderate degradation rate was achieved, while the 200 W lamp led to a rapid and substantial decrease in absorbance, signifying higher degradation efficiency.

This enhanced performance at increased intensities is likely due to the higher photon availability, which boosts the production of reactive species like hydroxyl radicals (•OH). These radicals are essential in the oxidative degradation of MB. Additionally, stronger illumination enhances the excitation of photocatalysts or enables more efficient direct photolysis, thus accelerating the degradation process.These results are consistent with previous studies, which have demonstrated that higher light intensities significantly enhance the effectiveness of photocatalytic and photolytic degradation pathways [205]



(a) **(b)** **(c)**

FigureIII.9 : Effect of lamp intensity for the photodegradation of methylene blue ,75W(a),100W(b) and 200W(c)

V.Conclusion :

In this study, palladium nanoparticles supported on mesoporous silica (Pd-MCM-41) were successfully synthesized using *Lawsonia inermis* extract through a green, eco-friendly method. The nanocomposite was characterized using UV-Vis, XRD, TEM, and FTIR, confirming its structure and properties.

The effects of various parameters—such as pH, temperature, reaction time, and concentration—on nanoparticle formation were investigated. The material showed effective photocatalytic activity for the degradation of methylene blue, with performance influenced by catalyst dosage, dye concentration, and light intensity.

This work demonstrates a promising green approach for treating dye-contaminated wastewater using biosynthesized nanomaterials.

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Abstract :

The photocatalytic degradation of methylene blue (MB) was studied using Pd-MCM-41 nanocomposites as an efficient photocatalyst. Palladium nanoparticles were embedded in the MCM-41 structure to improve photocatalytic performance. The activity was tested under both UV and visible light. Parameters such as light intensity, dye concentration, and catalyst dose were optimized. The degradation efficiency was tracked over several cycles to assess stability and reusability. Pd-MCM-41 showed superior performance compared to conventional photocatalysts. These results highlight its potential for wastewater treatment and the removal of organic pollutants.

Resumé :

L’étude a porté sur la dégradation photocatalytique du bleu de méthylène (BM) à l’aide de nanocomposites Pd-MCM-41. Des nanoparticules de palladium ont été intégrées à la structure MCM-41 pour améliorer l’efficacité catalytique. L’activité a été testée sous irradiation UV et visible. Les effets de l’intensité lumineuse, de la concentration en BM et de la quantité de catalyseur ont été étudiés. La stabilité et la réutilisabilité du catalyseur ont été évaluées sur plusieurs cycles. Pd-MCM-41 a montré de meilleures performances que les photocatalyseurs classiques. Ces résultats confirment son potentiel pour le traitement des eaux usées..

ملخص:

كمحفز ضوئي Pd-MCM-41 باستخدام المركب النانوي (MB) تمت دراسة التحلل الضوئي لصبغة الميثيلين الأزرق
لتحسين الأداء التحفيزي. جرى تقييم النشاط تحت MCM-41 فعال. تم تضمين جسيمات البلاديوم النانوية داخل هيكل
والضوء المرئي. تم تحليل تأثير شدة الضوء، وتركيز الصبغة، وكمية المحفز على كفاءة التحلل. تمت مراقبة UV إشعاع
كفاءة أعلى من المحفزات Pd-MCM-41 التفاعل عبر عدة دورات لقياس الاستقرار وقابلية إعادة الاستخدام. أظهر
التقليدية. تؤكد النتائج إمكانيته في معالجة مياه الصرف وإزالة الملوثات العضوية.