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Dedication

Dedication

*I dedicate the fruit of my efforts to those whom **Allah** has commanded me to honor and treat well, my dear parents. May God prolong their lives and grant them health and well-being.*

To those with whom we shared a home and who were our greatest support, my dear siblings, each by name, and a special mention to the companions of the journey who have left us, their words still echoing in our ears.

To everyone who taught me a letter throughout my academic journey and did not hold back their generosity, my esteemed teachers, each by name and rank.

To the students of knowledge, researchers, and readers who tread the paths of knowledge with passion and patience, hoping from the Almighty that this work will be a light to illuminate their way.

Finally, I ask Allah that this work be sincere for His noble face, beneficial to His servants, and accepted in the balance of my good deeds.

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Abstract

ملخص

Résumé

Abstract

Considered heavy metals, such as As(III), Be(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II), and Zn(II), in wastewater from petrochemical industries (oil and gas production plants) are a major concern in environmental toxicology due to their toxic effects on aquatic and terrestrial life. To preserve biodiversity, hydrosphere ecosystems, and human health, it is critical to remove these heavy metals from the watery environment. In this study, ZnO nanoparticles (NPs) were synthesized by a co-precipitation method , polyvinylpyrrolidone-coated ZnO nanocomposites (ZnO@PVP NCs) and characterized using UV-Vis spectrophotometry, FTIR spectroscopy, and X-Ray Diffraction (XRD) techniques, to investigate their optical properties, chemical structure, and crystalline structure. ZnO NPs exhibited an absorption peak at 311 nm and a bandgap of 1.94 eV, while ZnO@PVP NCs showed peaks at 311 nm and 361 nm with a reduced bandgap of 1.81 eV, and crystallite sizes of 22.84 ± 3.49 nm and 26.37 ± 2.90 nm, respectively. These were then used as adsorbents for the removal of As(III), Bi(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II), and Zn(II) from wastewater, achieving removal efficiencies exceeding 99.9% under optimal conditions, with ZnO@PVP NCs showing slightly enhanced performance for Cd, Mn, and Ni.

Keywords: *Heavy metals; ZnO nanoparticles; ZnO@PVP nanocomposites; wastewater treatment; adsorption; petrochemical industry*

Résumé

Les métaux lourds, tels que As(III), Be(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II) et Zn(II), présents dans les eaux usées des industries pétrochimiques (installations de production de pétrole et de gaz), constituent une préoccupation majeure en toxicologie environnementale en raison de leurs effets toxiques sur la vie aquatique et terrestre. Pour préserver la biodiversité, les écosystèmes de l'hydrosphère et la santé humaine, il est crucial d'éliminer ces métaux lourds des milieux aqueux. Dans cette étude, des nanoparticules de ZnO (NPs) ont été synthétisées par la méthode de co-précipitation, et des nanocomposites de ZnO enrobés de polyvinylpyrrolidone (ZnO@PVP NCs) ont été caractérisés à l'aide de la spectrophotométrie UV-Vis, de la spectroscopie FTIR et de la diffraction des rayons X (DRX) pour analyser leurs propriétés optiques, leur structure chimique et leur structure cristalline. Les nanoparticules de ZnO ont présenté un pic d'absorption à 311 nm et une bande interdite de 1,94 eV, tandis que les ZnO@PVP NCs ont montré des pics à 311 nm et 361 nm avec une bande interdite réduite de 1,81 eV, et des tailles de cristallites de 22,84 ± 3,49 nm et 26,37 ± 2,90 nm, respectivement. Ces matériaux ont ensuite été utilisés comme adsorbants pour l'élimination des métaux lourds As(III), Bi(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II) et Zn(II) des eaux usées, atteignant des rendements d'élimination supérieurs à 99,9 % dans des conditions optimales, les ZnO@PVP NCs montrant une performance légèrement améliorée pour Cd, Mn et Ni.

Mots-clés : Métaux lourds ; nanoparticules de ZnO ; nanocomposites ZnO@PVP ; traitement des eaux usées ; adsorption ; industrie pétrochimique

ملخص

تُعتبر المعادن الثقيلة، مثل As(III)، Be(II)، Cd(II)، Cr(VI)، Mn(II)، Mo(II)، Ni(II)، Pb(II)، Sb(III)، Se(−II)، وZn(II)، الموجودة في مياه الصرف الصناعي الناتجة عن الصناعات البتروكيماوية (مصانع إنتاج النفط والغاز)، مصدر قلق رئيسي في علم السموم البيئية بسبب تأثيراتها السامة على الحياة المائية والبرية. لحماية التنوع البيولوجي، ونظم الإيكولوجية المائية، وصحة الإنسان، من الضروري إزالة هذه المعادن الثقيلة من البيئة المائية. في هذه الدراسة، تم تصنيع جسيمات أكسيد الزنك النانوية (ZnO NPs) بطريقة الترسيب المشترك، وتم تحضير مركبات أكسيد الزنك النانوية المغلفة ببولي فينيل بيروليدون (ZnO@PVP NCs) وتوصيفها باستخدام تقنيات التحليل الطيفي بالأشعة فوق البنفسجية والمرئية (UV−Vis)، والتحليل الطيفي بالأشعة تحت الحمراء (FTIR)، وانحراف الأشعة السينية (XRD) لدراسة خصائصها البصرية، وتركيبها الكيميائي، وبنيتها البلورية. أظهرت جسيمات أكسيد الزنك النانوية قمة امتصاص عند 311 نانومتر وفجوة طاقة قدرها 1.94 إلكترون فولت، بينما أظهرت المركبات النانوية ZnO@PVP قمم امتصاص عند 311 نانومتر و361 نانومتر مع فجوة طاقة مخفضة قدرها 1.81 إلكترون فولت، وأحجام بلورية تبلغ 22.84 ± 3.49 نانومتر و26.37 ± 2.90 نانومتر، على التوالي. تم استخدام هذه المواد كمواد ماصة لإزالة المعادن الثقيلة As(III)، Bi(II)، Cd(II)، Cr(VI)، Mn(II)، Mo(II)، Ni(II)، Pb(II)، Sb(III)، Se(−II)، وZn(II) من مياه الصرف، محققة كفاءات إزالة تزيد عن 99.9% في الظروف المثلى، مع أداء محسن قليلاً للمركبات النانوية ZnO@PVP في إزالة الكادميوم، والمنجنيز، والنيكل.

الكلمات المفتاحية: *المعادن الثقيلة؛ جسيمات أكسيد الزنك النانوية؛ المركبات النانويةZnO@PVP ؛ معالجة مياه الصرف؛ الامتصاص؛ الصناعة البتروكيماوية.*

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List of Abbreviations

NPs :	Nanoparticles
NM :	Nanomaterials
nm :	Nanometers
ZnO :	zinc oxide
PVP :	poly vinylpyrrolidone
BC :	Before Christ
AC :	After Christ
NPs :	Nanoparticles
ISO :	International Organization for Standardization
Fe_2O_3 :	iron oxide
TiO_2 :	titanium oxide
AOP :	advanced oxidation process
eV :	Electron volt
QDs :	Quantum dots
MCM -41:	Mobil composition of matter.41
MCM -48	Mobil composition of matter.48
SBA-15 :	Santa Barbara amorphous
MOF :	metal-organic frameworks
AgS :	Silver Sulfate
FeS :	Iron sulfate
CuS :	Copper Sulfide
ZnO@PVP:	Zinc oxide coated with polyvinylpyrrolidone
NC :	Nanocomposite
UV-Vis :	Ultraviolet and visible spectroscopy
FTIR :	Fourier-transform infrared spectroscopy
XRD :	X-ray diffraction
USEPA :	The United States Environmental Protection Agency

General Introduction

General Introduction

Nanotechnology involves the study and engineering of materials at the nanoscale, where dimensions range from 1 to 100 nanometers. At this scale, materials exhibit unique properties that significantly differ from their bulk counterparts, enabling diverse applications across multiple fields [1], [2]. The term "nano" derives from the Greek word "nanos," meaning dwarf, and refers to dimensions on the order of one billionth of a meter. Nanomaterials possess distinct mechanical, thermal, chemical, and biological properties due to their high surface-area-to-volume ratio and quantum effects, distinguishing them from their parent materials [1], [3].

Owing to their elevated surface-area-to-volume ratio, nanomaterials exhibit enhanced molecular-level reactivity, resulting in distinctive electrical, optical, chemical, and mechanical properties compared to bulk materials [4]. These attributes make nanomaterials a focal point of extensive research due to their academic significance and technological potential across various disciplines. Nanostructures can be synthesized using diverse methods, including mechanical, chemical, and other techniques, tailored to specific applications [2].

Conversely, wastewater represents a major source of environmental pollution due to its diverse contaminants, including heavy metals such as lead and mercury. These metals are highly toxic, resistant to degradation, and pose significant risks to human health and ecosystems [5]. Consequently, developing effective technologies for their removal has become imperative.

Recent studies have demonstrated that nanomaterials offer innovative solutions for environmental remediation. Among these, zinc oxide (ZnO) nanoparticles stand out due to their high surface area, exceptional adsorption and catalytic properties, and potential for sustainable environmental applications [6]. In this study, ZnO nanoparticles coated with polyvinylpyrrolidone (PVP) were utilized as a novel catalyst for removing heavy metals from wastewater, representing a promising advancement in modern environmental treatment strategies.

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CHAPTER I

Theoretical Foundations of Catalysis and Industrial Wastewater Treatment

I.1. Overview of Nanomaterials:

Nanotechnology is the alteration or creation of materials at the atomic or molecular level. The phrase "nanoscale" derives from the Greek word "Nanos." meaning "dwarf." The nanoscale is commonly measured in nanometers (billionths of a meter). Materials made at this scale often have unique physical and chemical properties due to quantum mechanical phenomena [1]. The processing and control of nanoscale materials satisfies human imagination in a variety of disciplines. Nanomaterials include a wide variety of materials with diameters ranging from 1 to 100 nm (**Figure (I.1)**). Materials at the nanoscale have unique features when compared to their previous states, and they are more chemically reactive due to their large specific surface area.

Over the next few years, the integration of a comprehensive set of engineering disciplines and basic sciences, including physics, chemistry, biology, and materials science, could significantly contribute to the application and use of nanomaterials in a variety of fields, including computer chips, energy, healthcare and medical diagnostics, and the aerospace industry.

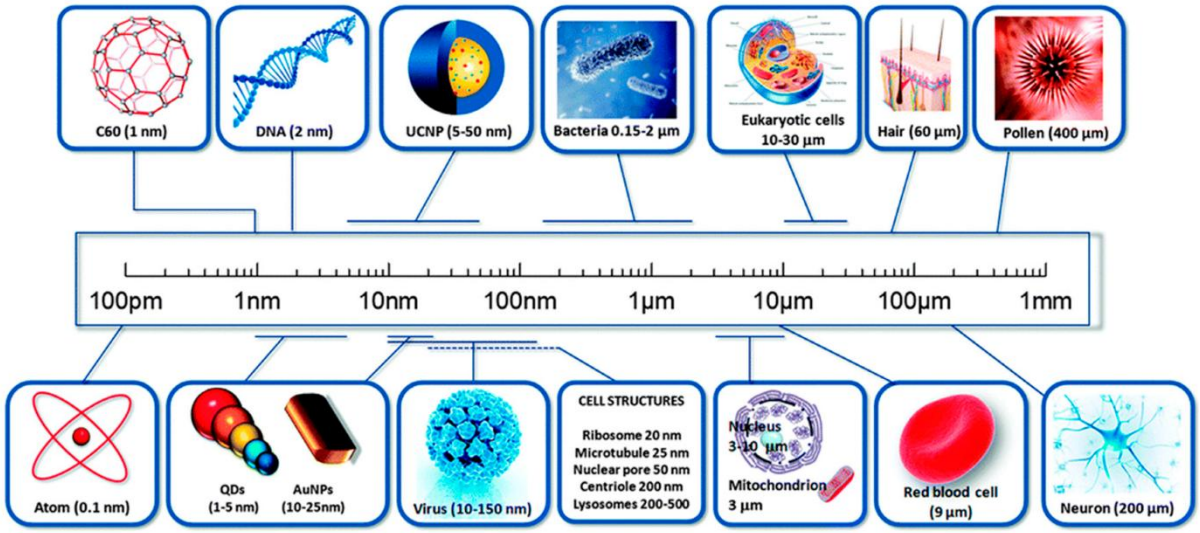

Figure (I.1): *Concept on length scale showing size of nanomaterials and their comparison to biological components and the definition of 'micro' and 'nano' sizes* [2].

I.1.1 History:

Nanomaterials have a long-standing and close association with the evolution of life on Earth, as fire residues, volcanic ash, and radioactive decay are among the most important natural sources of these materials**.** Nanomaterials and their derivatives have been created and used since

prehistory. Nanotechnology characterization tools have advanced significantly, allowing researchers to investigate their origins and analyze their effects on the Earth's ecosystem and human health [3].

Nanotechnology today is the result of breakthroughs spanning multiple historical periods, including prehistory, ancient ages, the Middle Ages, and modern and contemporary eras. **Figure (I.2)** illustrates the evolution of nanotechnology over time. The contemporary period in nanotechnology began in 1959 with Richard Feynman's lecture, "There's Plenty of Room at the Bottom," which marked the start of modern nanotechnology, with significant advancements emerging in the 1960s.

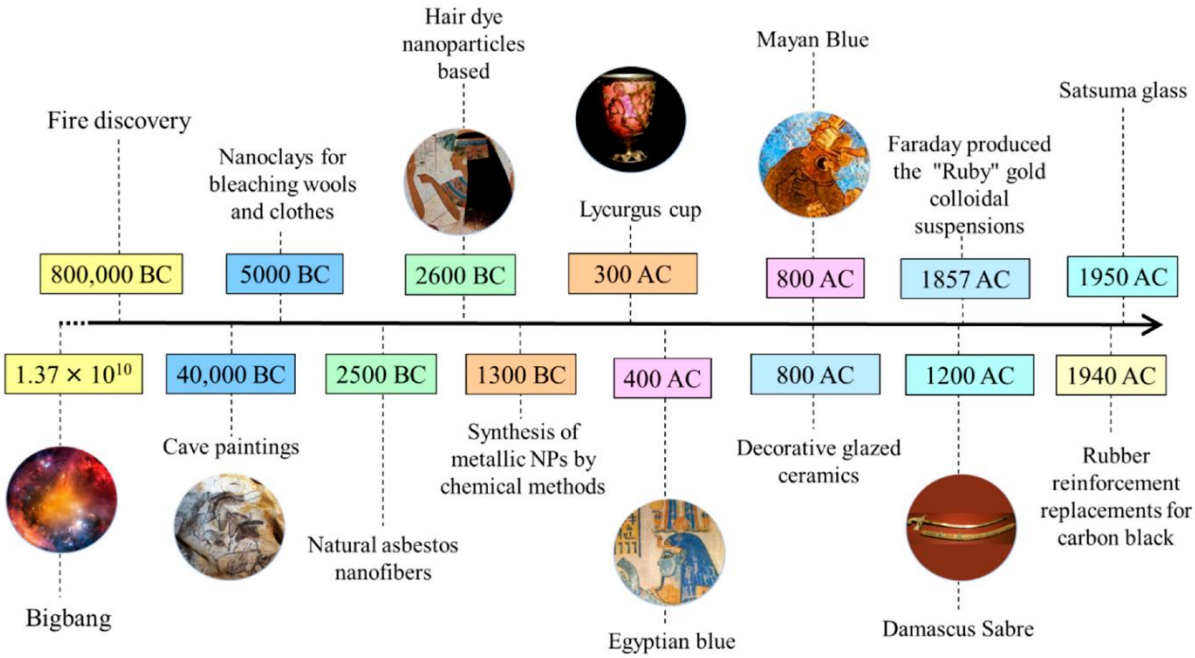

Figure (I.2): *Timeline summarizing ancient civilizations; they produced and used nanomaterials without knowing their nanosized characteristics* [4].

I.1.1.1 Prehistoric Nanomaterials:

These eras were characterized by the poor and random use of nanomaterials without knowledge of them or their properties.

Humans used carbon combustion residues and wax in cave paintings during these times. The hand-drawn images in the caves of Sulawesi, Indonesia, are among the oldest examples of this. Carbon dating results have shown that these paintings were made around 40,000 years BC using fats, charcoal, and plant pigments. Similar drawings can also be found in France's Chauvet-Pont d'Arc Cave, which dates from 340,000 BC. These analyses have revealed that humans unknowingly used nanomaterials such as graphene (**Figure (I.3)**)[3].

Figure (I.3): Ancient Paintings in Chauvet-Pont-d'Arc and Lascaux caves containing nanostructures. © MCC/DRAC. Open Access.

I.1.1.2 Nanomaterials and Ancient Civilizations:

The Greeks and Egyptians used nanomaterials in synthetic chemical processes to create nanostructured hair dye (**Figure (I.4) A**). The Egyptians invented the oldest synthetic color , "Egyptian blue," in the third century, which is a finely decorated mixture of glass and quartz (**Figure (I.4) B**) [5]. Natural nanomaterials were employed as early as 5000 BC,

The Maya civilization in America produced pigment compounds (including blue), and interestingly, Egyptian blue differs from the blue pigments produced by other civilizations in Europe and Asia.

Metallic nanoparticles are also attributed to the Mesopotamians and Egyptians in the twelfth and fourteenth century BC. The most well-known example is the use of metallic nanoparticles in

Roman glass. Dichroic glass, used to produce the Lycurgus Cups, a form of Roman glass cup from the fourth century, changes color depending on the sort of light it is exposed to.

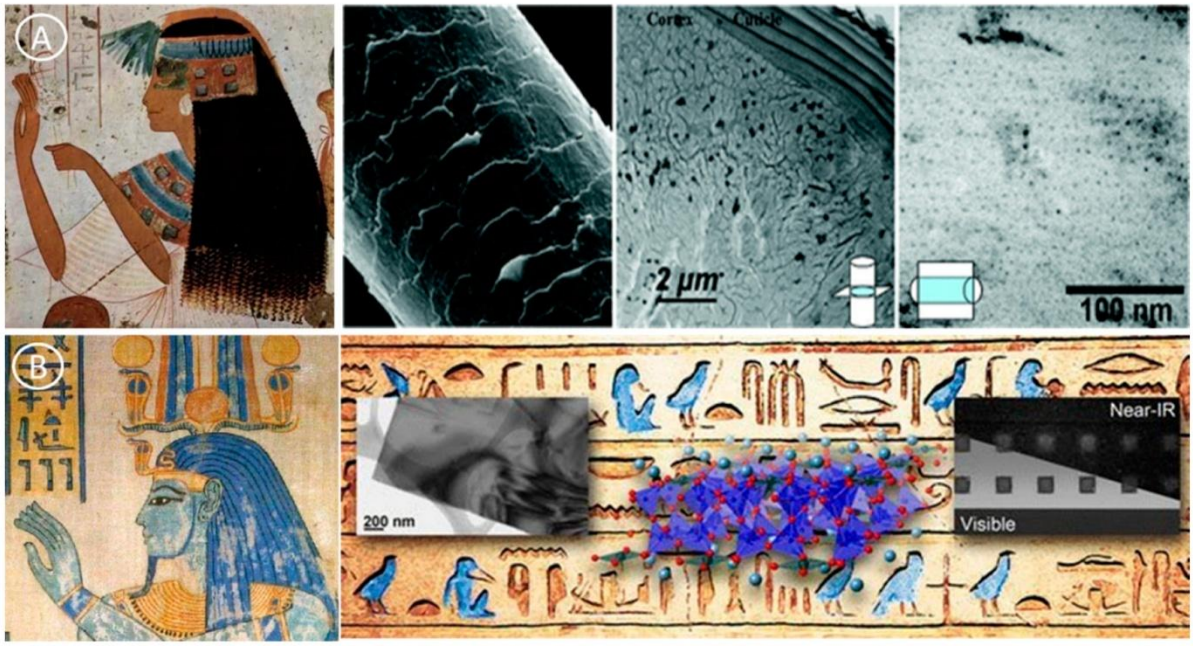

Figure (I.4) : Nanomaterials produced by humans in ancient civilization: (**A**) Egyptians produced PdS_2 NPs as a dye for hair [6],(**B**) Egyptians produced Egyptian blue ($CaCuSi_4O_{10}$ and SiO_2, nanosheets of less than 5 nm in thickness) [7].

I.1.1.3 Nanomaterials in Medieval Times:

The Romans' use of nanoparticles, especially metallic NPs, and nanostructures is a noteworthy example of early nanotechnology knowledge. The Lycurgus cup (**Figure (I.5) A**) is the oldest known dichroic glass, displaying two distinct hues when exposed to various light wavelengths. It serves as an amazing example of Roman glass manufacture. The Lycurgus cup appears green in direct light and red-purple when lit from behind (**Figure (I.5) A**) [8]. Electron microscopy and X-ray diffraction (XRD) investigations reveal that color duality is caused by nanoparticles (of gold and silver) with diameters ranging from 50 to 100 nm.

Islamic countries also witnessed a widespread use of shiny pottery. Elemental analysis of these ceramic decorations revealed the presence of nanoparticles of silver and copper. Furthermore, Damascus steel was used in the 13th century to manufacture blades, as this steel contained nanowires to provide strength and durability (**Figure (I.5) B**)[3].

Figure (I.5): Examples for some handmade nanomaterials used in medieval times. (**A**) The Lycurgus cup is brilliant red when light passes through the glass that contains Au-Ag NP alloy [9]; (**B**) Saber made of Damascus steel (photograph by Tina Fine berg for The New York Times

I.1.1.4 Nanomaterials in the Modern Age:

Scientists are perplexed by the unique properties of these old relics, prompting them to reconsider them. In the mid-nineteenth century, 1857 Michael Faraday studied the creation of colloidal gold "ruby" and established that gold nanoparticles may change the color of a solution under specific lighting circumstances [10]. In the 1940s, silica nanoparticles were manufactured as alternatives to strengthen black rubber. Feynman's "There's Plenty of Room at the Bottom" talk at the American Physical Society's annual conference on December 29, 1959, launched a brand-new field called "nanotechnology." A small group of scientists, including Richard Zsigmondy, coined the term "nanometer" to describe the measurement of colloidal gold dimensions in the early 1960s and were forecasting the future of nanoscience ("the future of the nano") The numerous recent advancements in nanomaterials are depicted in (**Figure (I.6))** [3].

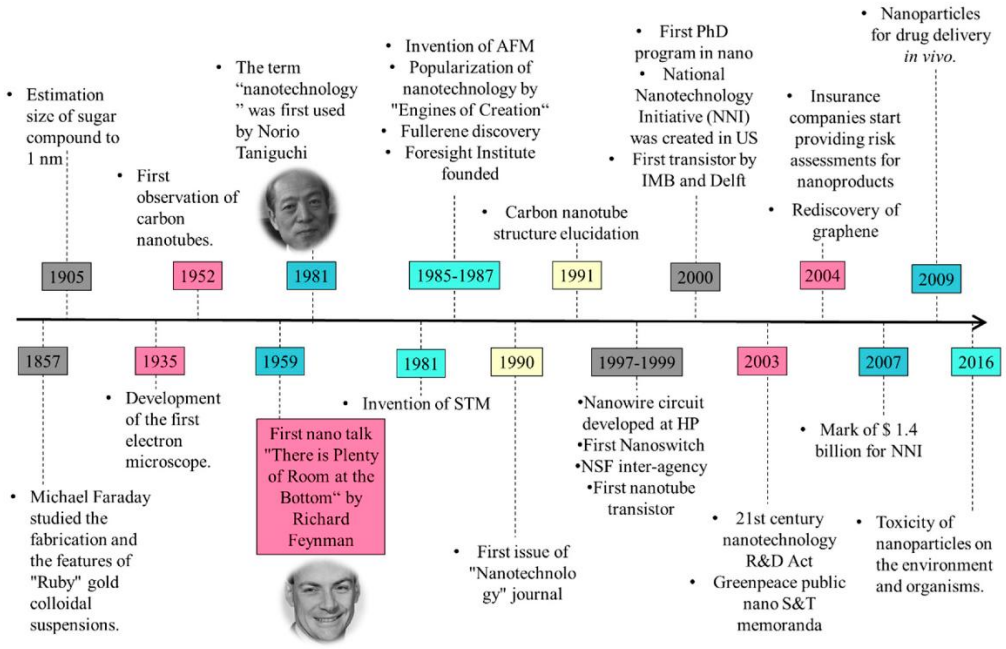

Figure (I.6) : *Timeline of nanomaterials discovery in the modern nanotechnology era [4].*

I.1.2. Terms related to nanotechnology:

The word "nano" which means dwarf, is connected with a wide range of concepts. As a result, the International Organization for Standardization (ISO) defines nanomaterials as any substance with an internal or exterior dimension on the nanoscale. **Table (I.1)** explains a variety of terms linked to the term nano [1].

Table (I.1): *Various terms associated with the term "nano"*

Terms	Size and Explantation
Nanoscale	Size range between 1 to 100 nm
Nanoscience	Nanoscience involves investigation and understanding of matter at the nanoscale where the properties of the materials are completely different as compared to bulk materials.
Nanotechnology	It is the technology involving in developing materials, devices or systems by controlling matter at nanoscale.
Nanomaterial	Any material having at least one dimension in the nanoscale range of 1 to 100 nm.
Nano object	It is a material with one, two or three external dimensions in the nanoscale range
Nanoparticle	A material for which all three dimensions are in nanoscale range

Nanofibre	It is a nano object for which any two dimensions are in nanoscale range while the third dimension is significantly larger in size.
Nanostructure	The material with discrete functional parts in which the internal or surface structure is at least one of them in nanoscale region.
Nanocomposite	Multicomponent having multiphase domains in which at least one of the phases has a minimum of one dimension in nanoscale region.
Nanorod	The materials in which the shortest and longest axes are lengthwise different. The width of nanorods is between 1-100 nm and aspect ratio more than one.
Nanowire	Nanowire is similar to nanorod, only difference being their aspect ratio is very high.
Nanosphere	These are nanoparticle with aspect ratio of 1.
Nanotube	Nanotubes are basically hollow nanofibers
Nanostructured material	These are structured materials built by elements, molecules, crystallites or clusters in the nanoscale region.
Engineered nanomaterials	Anthropogenically created materials having one or more dimension in the range of 1-100 nm
Nonmanufacturing	It refers to the production of materials at nanoscale through top down and bottom-up approach

I.1.3. Metallic Nanoparticles:

I.1.3.1. Nanoparticles:

According to the ISO's definition of nanomaterials, nanoparticles are bodies with three exterior dimensions (length, width, thickness) that fall inside the nanoscale, specifically between 1 and 10 nm [1].

I.1.3.2. Metallics nanoparticles:

Metallic nanoparticles were discovered in 1908, when Faraday detected metallic particles in solution and Mai presented a quantitative explanation for their color[11]**.**

Metallic nanoparticles are tiny metals that range in size from 10 to 100 nm. Their physical and chemical characteristics are essentially dependent on relatively free electrons. They also have distinguishing traits such as high surface energy, efficient plasmon excitation, and excellent optical properties [9-10]. Metallic nanoparticles also act as catalysts for many chemical reactions.

I.1.3.2.1. Advantages of Metallic Nanoparticle:

- Strong plasma absorption
- Determine chemical information on metallic nanoscale substrate
- Biological system imaging
- Surface enhanced Raman scattering
- Enhance Rayleigh scattering [11].

I.1.3.2.2. Disadvantages of Metallic Nanoparticles

A) Particles instability: Nanomaterials can undergo metamorphosis due to their thermodynamic instability and location near high energy local minima. This causes quality degradation, poor corrosion resistance, and makes it difficult to maintain the structure.

B) Difficulty in synthesis: To maintain the size of nanoparticles in solution, they should be enclosed during the synthesis process.

C) Impurity: Impurities are formed during the synthesis of nanomaterials.

D) Explosion: Exothermic combustion can result in explosions due to the intense explosive properties of tiny metal particles [11].

I.1.3.3. Metal Nanoparticles as Catalyst:

Metallic nanoparticles operate as excellent catalysts for a wide range of chemical reactions; therefore, they must be stable when utilized as catalysts; otherwise; they will be ineffective. The benefits of employing metallic nanoparticles are as follows:

A) The temperature applied to the catalyst containing metallic nanoparticles distributed in solution is lower than the solvent's boiling point.
B) Metallic nanoparticles distributed in liquids act as photo catalysts due to their transparency to light.
C) Metallic nanoparticles mounted on solid supports works as catalysts even for the processes in a gaseous phase.
D) Bimetallic and trimetallic nanoparticles can be created by altering their structures and compositions [11].

I.1.3.4. Uses of metallic nanoparticles:

These particles' various and useful features have led to a proliferation of applications.

In Medicine: Nanoparticles, particularly metallic ones, operate as versatile agents with a wide range of medicinal and biological applications, resulting in a substantial revolution in both the medical and pharmaceutical industries. Metallic nanoparticles of gold and silver, for example, are employed for their therapeutic characteristics in the treatment of a variety of ailments [11].

In Water Treatment: Nanoparticles are seen as viable alternatives for cleansing and treating contaminated water, whether it be petroleum or sewage wastewater.

These particles have a variety of uses in physics, organic and inorganic chemistry, optical and electronic technology, and modern agricultural, feed, and food industries.

I.1.4. Properties of Nanomaterials:

Nanomaterials are materials with dimensions ranging from 1 to 100 nm that exhibit distinct properties when compared to their larger equivalents. These features result from their small size, large surface area, and quantum effects. The following sections outline the key properties of nanomaterials:

I.1.4.1. Catalytic Properties:

Catalysis is regarded as one of the main foundations of contemporary chemistry due to its high efficiency in turning raw materials such as gas and oil into valuable chemicals while consuming less energy and producing less waste. The science of catalysis has seen considerable advancements during the last century, and research is still underway to build more stable and active catalysts.

Catalysts are classified into two types: homogeneous (soluble molecular complexes) and heterogeneous (solid particles that may be anchored to another solid particle). Applying homogeneous catalysts in the same phase improves substrate access, leading to increased catalytic activity and selectivity. However, homogeneous catalysts have the drawback of separating the catalyst from the products. In contrast, in heterogeneous catalysis, the catalyst units are fixed to solid support materials, which aids in the separation process [13]. Nanocatalysis has gained prominence in chemistry because to its high activity and selectivity. Nanocatalysts have special features due to their nanoscale size, shape, and enormous surface area relative to volume, which

distinguishes them from bigger counterparts. The use of nanoparticles in catalysis is a pioneering application in the discipline. For years, catalysts in nanoscale have been used, including clays, silica, titanium dioxide, iron, and aluminum. However, the amazing catalytic activities of nanoparticles are still not fully understood [14].

Heterogeneous catalysis is one of the most prominent applications of nanomaterials in the field of catalysis due to its characteristic presence of a solid catalyst and a reactive liquid or gas phase. Intensive studies have been conducted on catalytic activity in chemical processes such as hydrogenation and oxidation on various nanomaterial-based catalysts, including noble metals (gold, silver, platinum) as well as metal oxides like zinc oxide(ZnO), iron oxide (Fe_2O_3), and titanium oxide(TiO_2).

Wang et al. (2019) [15] found that Pt-based nanoparticles supported on carbon nanotubes had better catalytic performance for selective hydrogenation of nitroaromatic compounds due to their great dispersion and strong metal-support contact.

Nanomaterials play a crucial role in energy conversion and storage devices including fuel cells, batteries, and electrolyzes, where they catalyze processes at electrode surfaces. Platinum nanoparticles, carbon nanotubes, and metal oxides have been studied for their catalytic activity in reducing oxygen, hydrogen, and carbon dioxide. ***Zhu et al. (2021)*** [16] found that nitrogen-doped carbon nanotubes supported by cobalt oxide nanoparticles had higher electrocatalytic activity for oxygen reduction in alkaline media. This highlights the potential of nanomaterials to improve electrochemical device performance and efficiency [17].

These benefits can improve the efficiency of industrial chemical operations, reduce energy consumption, and minimize waste formation. This can reduce the negative impact of chemical operations on the environment. Nanoparticles have a significant role as catalysts in various industrial applications, including chemical production, energy conversion, and storage. Nanoparticles vary in size and form, leading to diverse catalytic activity [14].

I.1.4.2. Antimicrobial properties:

Antibiotics are commonly used to treat bacteria, viruses, parasites, and the main fungus. Newer forms of antimicrobials must continue to be researched and developed. However, the rise of germs resistant to antimicrobials has become the most significant concern, particularly in light of the recent pandemic.

Recently, nanoparticles have emerged as a promising cure and alternative to medicines for combating antibiotic-resistant bacteria [18].

Metallic, polymeric, lipid, and carbon nanoparticles are characterized by unique properties in producing superoxide ions and hydroxyl radicals that eliminate antibiotic-resistant bacteria by disrupting membranes and inhibiting enzymes. Nanoscale particles (NPs) are being used to control bacterial infections as an alternative to antibiotics. Nanoparticles (NPs) are commonly used in antimicrobial coatings for implantable devices, medicinal materials, wound healing, bacterial detection, and antibiotic delivery systems. Nanomaterial-based therapeutics have the potential to treat severe bacterial infections and bypass drug resistance mechanisms.

Nanomaterials' unique size and physical features enable them to target biofilms and overcome persistent diseases.

Nanoparticles exhibit diverse shapes and are widely utilized in healthcare and medicine, particularly in antibacterial therapy. **Figure (I.7)** illustrates various types of antibacterial nanoparticles [19].

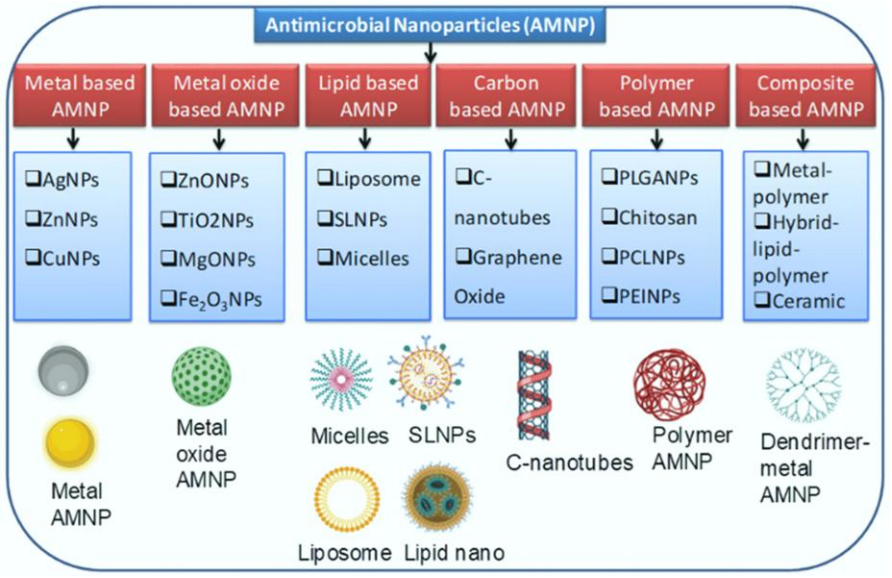

Figure (I.7): *Different types of antimicrobial nanoscale particles and their hypothetical illustrations* [20].

Nanoparticles' increased surface area enhances their antibacterial action. Nanoparticles have a larger surface area, which increases medication loading capacity and improves interactions with bacterial cells. Figure 8 represents the various advantages of nanoparticles in combating bacterial cells (**Figure (I.8)**) [19].

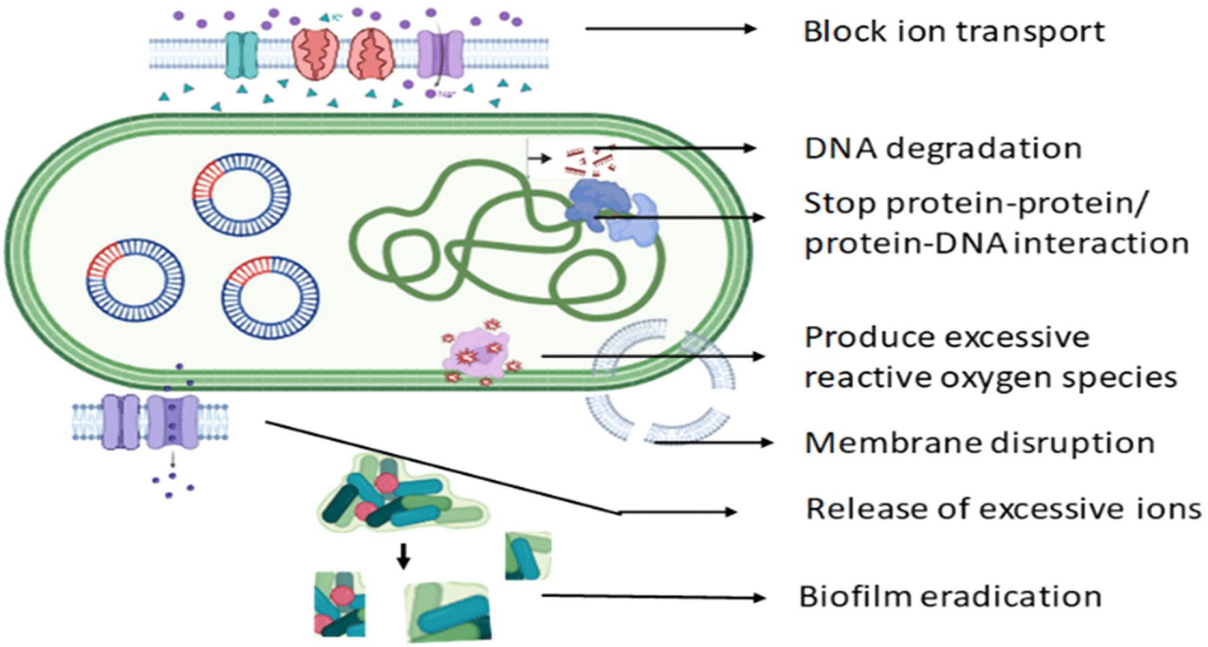

Figure (I.8): *Bactericidal effect of nanoparticles and their modes of action* [20].

I.1.4.3. Optical Properties:

Based on their size-tunable qualities, "nanomaterials" have emerged as the darling materials of the twenty-first century for a variety of practical applications, including optical. Optical qualities are among the most appealing and practical characteristics of nanomaterials, and they have been thoroughly investigated using a range of optical spectroscopic approaches. Anyone interested in studying nanomaterials, whether semiconductors, insulators, or metals, must first grasp their optical properties and related spectroscopic systems. This is due in part to the close relationship between optical properties and various characteristics and functions (such as electronic, thermal, and magnetic) that are critical in many mechanical applications, including sensing, optoelectronics, energy conversion and storage, solar cells, photocatalysis, photonic optics, and communications. Nanomaterial containment comprises a variety of approaches for controlling the dimensions and shape of the material within different ranges of nanostructures for optical applications. Nanoparticles, which have remarkable electrical and optical capabilities, can be employed to absorb UV rays in sunscreen creams.

Metallic nanoparticles have unique optical properties and enhanced electromagnetic (EM) fields, and their numerous consequences and applications have prompted a branch of research

known as "plasmonic." In 1857, Michael Faraday noticed the presence of metallic nanoparticles in solution. They have numerous uses in catalysis, imaging, sensing, and other research and technological domains. The most extensively studied metallic nanoparticles are gold and silver. Nanogold was employed in the early medieval period to stain Roman church glass windows, and the color-changing Lycurgus cup is made out of gold (Au) and silver (Ag) nanocrystals. The origin of this color can be explained with a method called surface plasmon resonance (SPR) (**Figure (I.9)**).

Metallic nanoparticles have a plasma composed of electrons that can resonate with a natural frequency determined by factors like material, shape, size, and the surrounding environment. Light waves, which are electrically and magnetically active, can displace the electron plasma cloud relative to the nanoparticle's nuclei. When a metallic nanoparticle meets incoming light waves, some energy is absorbed by the nanoparticles, causing oscillation of the plasma cloud. The energy absorption is maximum when the frequency of the incoming light radiation is the same as the natural frequency of the electron plasma. This collective absorption produces a color from the nanoparticle dispersion, with different colors emitted by nanoparticles of the same metal, with varying sizes and shapes [16-17].

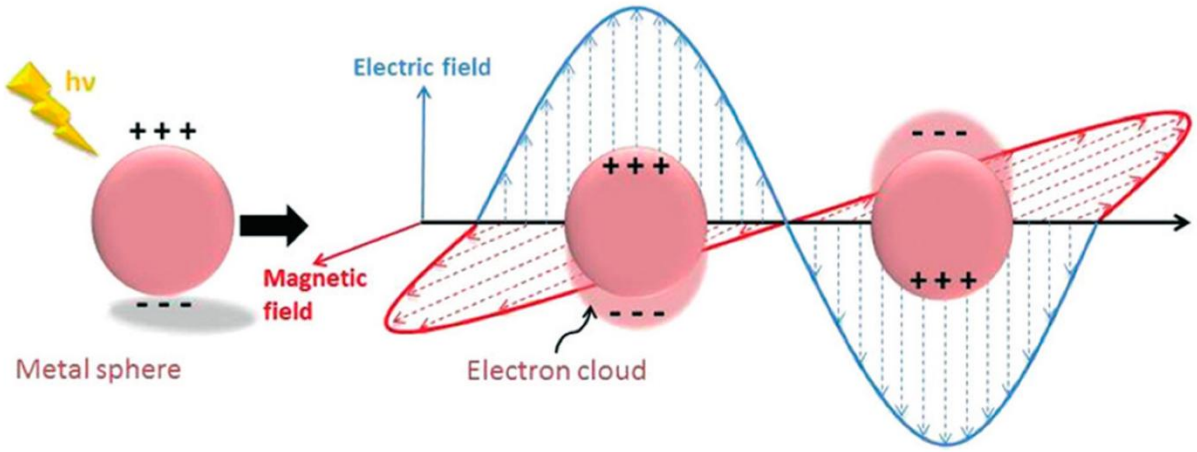

Figure (I.9): *Schematic illustration of a localized surface Plasmon resonance* [23].

I.1.4.4. Photocatalytic Properties:

Clean and potable water is a huge difficulty in this day and age since massive amounts of untreated industrial waste are being dumped into bodies of water, resulting in health crises that have raised alarms. There are numerous technologies for purifying and treating water, such as

reverse osmosis and ultrafiltration, but they only shift industrial waste from one state to another, thus the damage remains even after treatment. As a result, photocatalytic technologies are thought to be more effective at converting impurities into carbon-containing compounds.

Photocatalysis is an advanced oxidation process (AOP) that can be utilized to eliminate contaminants in a simple and effective manner. It is one of the most economical and promising industrial wastewater treatment methods. P-type semiconductor nanoparticles have been extensively examined for their effectiveness in removing organic dyes, toxic composites, and poisonous compounds from water using photocatalytic processes. Color pollutants are chemically stable, making UV radiation and hydrogen peroxide oxidation ineffective. However, photocatalytic methods using semiconductor nanomaterials have gained attention for their effectiveness in decolorizing dyes [24].

Metal oxide particles (11) have recently gained popularity as environmentally benign photocatalysts, thanks to their chemical stability, electron transfer capabilities, low cost, non-toxicity, and electrochemical catalytic characteristics. This p-type and n-type semiconductor metal oxide has an adjustable band gap in the range of 3.0-4.0eV, depending on the nature of defects and density. Due to their broad band gap and strong photosensitivity [24].

In the photocatalytic reaction, the semiconducting photocatalyst absorbs light energy that is greater than the band gap, resulting in the formation of a hole and electrons, which in turn produce efficient oxidizers of organic dyes. Because of the rapid recombination of photo-induced CB electrons and VB holes, it is difficult to get efficient degradation efficiency employing semiconductor photocatalyst from aqueous solution. In the case of dye pollutants, the dye works as a photosensitizer in visible light, while an excited electron is injected into an electron acceptor and transformed to a cationic dye radical ($dye^{\cdot+}$), which then degrades or decomposes itself. This photocatalytic degradation process for dyes differs from the standard semiconductor photocatalysis under UV irradiation and has been shown to be an efficient approach to remove textile dyestuff from aquatic environments [24]. (**Figure (I.10)**) shows various nanomaterials used as photocatalysts.

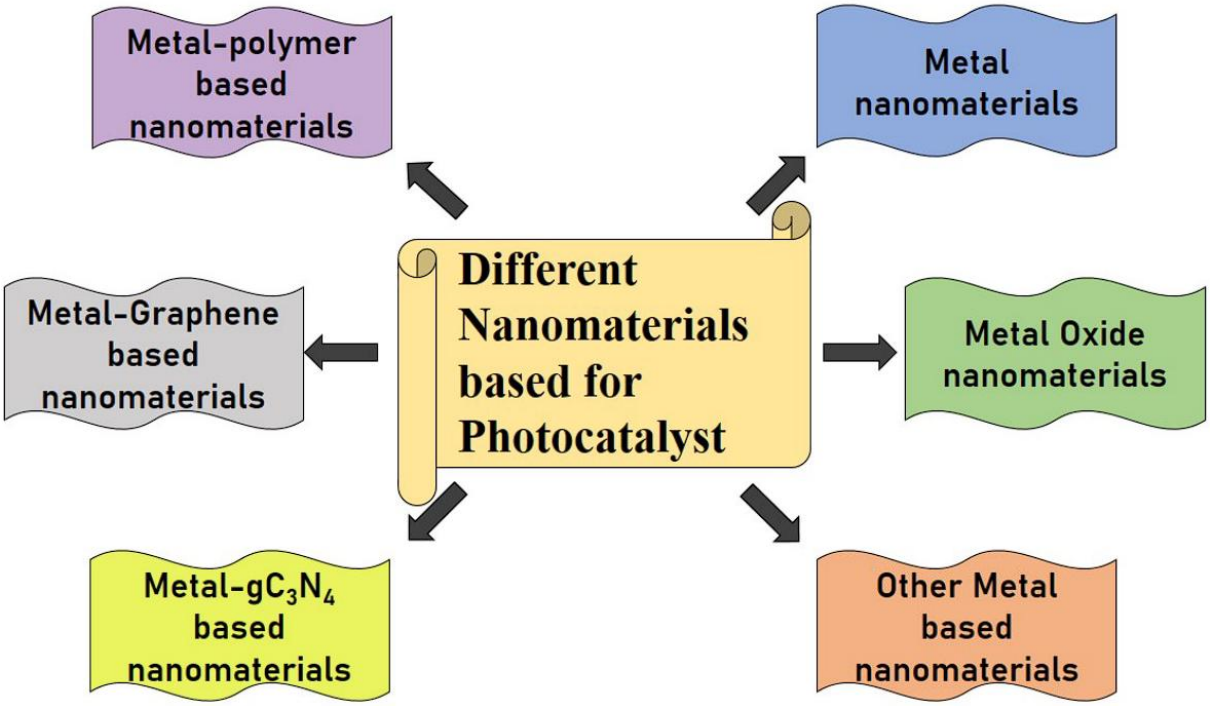

Figure (I.10): *Different nanomaterials used as photocatalyst* [24].

I.2. Types and Classification of Nanomaterials:

NMs can be classified into four broad types, regardless of their location or chemical properties.

I.2.1. Classification of nanomaterials based on origin:

Natural and artificial nanoparticles are the two groups into which nanomaterials are divided based on origin

a) Natural nanomaterials: Natural nanomaterials exist in a variety of forms, including viruses, proteins, minerals, colloids, fog, gelatin, and mineralized materials [25].

b) Artificial nanomaterials: Carbon nanotubes and semiconductor nanoparticles, such as QDs, are synthetic nanomaterials made using precise mechanical and manufacturing techniques [25].

I.2.2. Classification of nanomaterials based on the structural configuration/composition:

Nanoparticles are classified into four types based on their structure: organic/dendrimers, inorganic, carbon-based, and composite**.**

a) Organic nanomaterials: On the nanoscale, organic compounds are converted into organic nanomaterials [25]. As show in (**Figure (I.11)**).

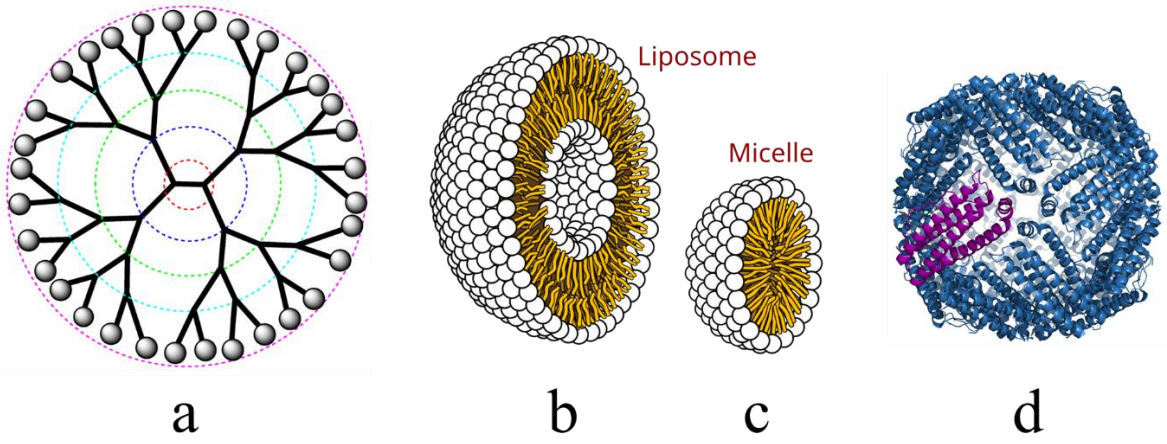

Figure (I.11): *The examples that follow consist of organic nanomaterials: (a) Dendrimers (b) Liposomes and (c) Micelles (d) Ferritin* [26].

b) Inorganic nano materials: Inorganic nanoparticles, which lack carbon atoms, are usually made of metal-based or metal oxide-based nanomaterials [25].

c) Carbon based nanomaterials: Carbon-based nanomaterials are constituted of five primary materials: carbon nanotubes, graphene, fullerenes, carbon nanofiber, and carbon black. Fullerenes, which have a spherical or ellipsoidal shape, are sometimes known as Bucky balls. Fullerenes are spherical structures with diameters of up to 8.2 nm for a single layer and 4 to 36 nm for multi-layered fullerenes, formed by 28 to 1500 carbon atoms [25].

d) Composites nanomaterials: Composites Nanomaterials are a combination of nanoparticles, larger-scale materials, and bulk materials. Nanomaterials improve mechanical, thermal, and flame-retardant qualities in a variety of items, including vehicle parts and packaging materials [25].

I.2.3. Classification of nanomaterials according to the number of dimensions:

a) Zero-dimensional nanomaterials: Nanomaterials with three dimensions within the nanoscale range (10-100nm).

b) One-dimensional nanomaterials: Nanomaterials in this category have two of their three dimensions at the nanoscale.

c) Two-dimensional nanomaterials: Two-dimensional nanomaterials outside the nano range and one-dimensional within the nano scale

d) 3D nanomaterials: are non-nanoscale materials with several dimensions, a 3D substance has dimensions beyond the nanoscale range (100 nm or higher).

I.2.4. Classification of nanomaterials based on pore dimensions:

Nanomaterials are divided into three types based on their diameter dimensions: microporous, mesoporous, and macroporous. Pore diameter affects molecule size, transport, and interaction qualities. When guest molecules are smaller than the pore size, they interact less with the wall and more with other molecules during diffusion. These parameters are crucial for adsorption and diffusion applications [25].

a) Microporous materials: Microporous materials contain pores with widths smaller than 2nm. They may only include tiny molecules like gasses or linear molecules.

They exhibit sluggish diffusion kinetics and high interaction characteristics. Microporous materials include Na-Y and naturally occurring clay. They are utilized in gas purification systems, membrane filters, and gas storage materials [25].

b) Mesoporous materials: Mesoporous materials, including MCM 41, MCM-48, SBA-15, and carbon mesoporous materials, have large pores that can accommodate molecules larger than 2nm but smaller than 50nm [25].

c) Macroporous materials: Carbon microtubes, porous gels, and porous glasses are examples of macroporous materials with pores larger than 50nm, which may accommodate large molecules and serve as matrices, scaffolds, and sensing materials [25].

(**Figure (I.12)**) categorizes nanomaterials based on their size, origin, structure, pore size, and possible toxicity.

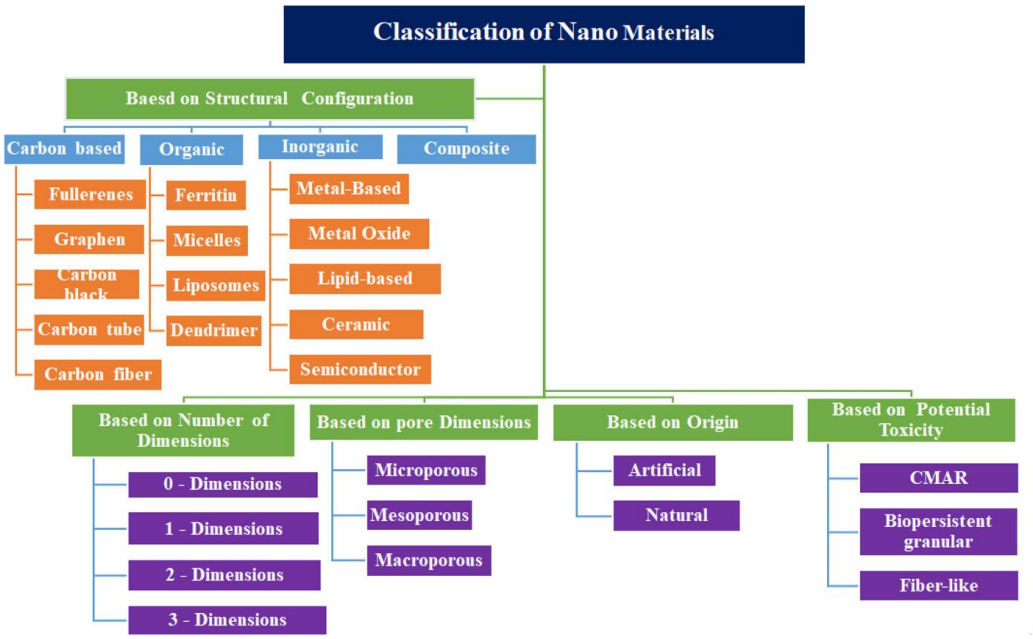

Figure (I.12): *General classification of nanomaterials* [25].

I.3. Metallic Nanoparticles:

Metal nanoparticles, or submicron-sized objects, are made from pure metals such as gold, zinc, platinum, silver, iron, titanium, cerium, and thallium, as well as their compounds such as oxides, hydroxides, fluorides, sulfides, phosphates, and chlorides. The term "metal nanoparticle" refers to nanosized metals with length, breadth, or thickness measures of 1 to 100 nm. Metal nanoparticles (e.g. silver, copper, gold, magnesium, iron, titanium, palladium, platinum, zinc, and alginate) are the first class of nanomaterials. Other nanomaterials include metal oxide and metal sulfide nanoparticles like zinc oxide, titanium dioxide, zinc sulfide, and others. Metal, doped metal, metal oxide, and metal sulfide nanoparticles are distinct types of nanomaterials.

Nanomaterials composed of metal sulfide and metal-organic frameworks (MOFs) have sparked widespread interest due to their fascinating properties and prospective applications in a variety of biological areas. This contains AgS, FeS, CuS nanoparticles, Cu-based, Mn-based, and Zn-based MOFs, among other compounds. These compounds are commonly employed in medicinal applications, including drug development and antibacterial activities [27].

I.3.1. Zinc Oxide (ZnO) Structure:

Zinc oxide (ZnO), an ancient substance, has been regaining popularity in the scientific world since the 1990s. This is a very remarkable substance with unique features. ZnO was formerly

employed in paint, phosphorescent, UV-blocking, and culinary applications. However, this inexpensive material with a stable wurtzite structure exhibits distinct electrical, photonic, and piezoelectric capabilities in a single configuration. It is gas/pressure sensitive and may function as a nonlinear varistor and sensor [8]. Piezoelectric ZnO is used in surface and bulk acoustic wave devices. It is a semiconductor with a broad band gap of 3.37 eV at ambient temperature and a high exciton energy of 60 meV, making it a valuable functional oxide in optics and optoelectronics [28]. ZnO nano powders have been synthesized using several techniques, including the organometallic precursor method, microemulsion synthesis, sol-gel process, PVD (Physical Vapour Deposition), precipitation, chemical vapor deposition, chemical bath deposition, solvothermal, and hydrothermal processes [29].

Because zinc and oxygen are in the second and sixth groups of the periodic table, respectively, ZnO is a recognized II VI semiconductor in materials science. The ZnO semiconductor offers several unique and advantageous qualities, including good transparency, antibacterial agents, high electron mobility, a broad bandgap, great thermal and mechanical stability at room temperature, and strong room temperature luminescence. Its huge bandgap, or 3.37 eV, is on the boundary between ionic and covalent semiconductors. ZnO's crystal structure is wurtzite (B4), with a hexagonal unit cell and two lattice parameters of a = 0.325 nm and c = 0.521 nm. With its hexagonal wurtzite structure, each anion is surrounded by four cations in the corners of the tetrahedron, demonstrating tetrahedral coordination and so sp3 covalent bonding. ZnO's tetrahedral form leads to a non-centrosymmetric structure (**Figure (I.13)**) [30].

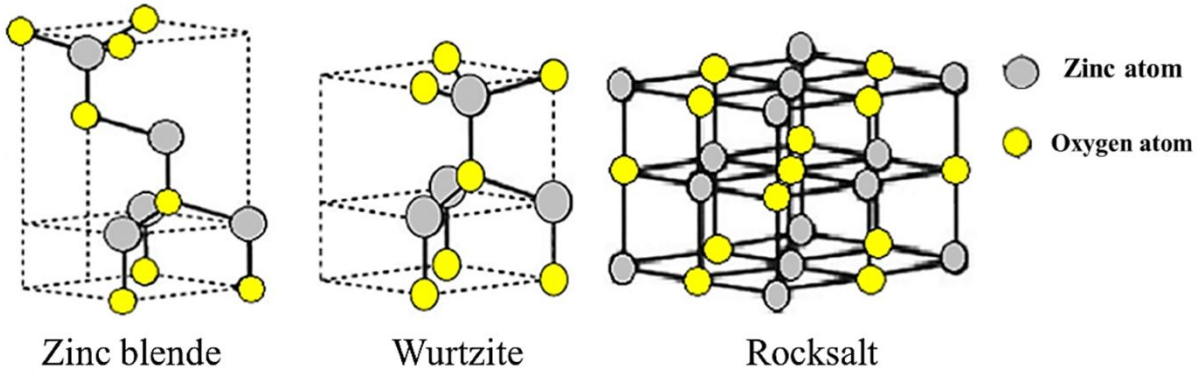

Figure (I.13): *Crystal structure of ZnO in wurtzite, rocksalt and zinc blende* [31].

I.4. General Overview of PVP (Polyvinylpyrrolidone):

Polyvinylpyrrolidone (PVP), often known as Povidone, is a synthetic polymer formed by radical polymerization of the monomer N-vinylpyrrolidone. In 1939, German scientist Walter J. Reppe patented this technique based on his acetylene chemistry research. PVP is nontoxic, non-ionic, inert, temperature-resistant, pH-stable, and biocompatible, with a complicated affinity for hydrophilic and hydrophobic medicines. PVP is a water-soluble polymer that comes in several grades with differing molecular weight and viscosity. PVP was first employed in the 1940s to increase plasma volumes. In the 1950s, PVP supplanted shellac glue as a hair fixative.

Later, PVP proved valuable in the pharmaceutical, biological, cosmetic, and food industries. PVP's unusual features and chemistry have led to breakthroughs in its synthesis into several kinds, including homopolymers, copolymers, and crosslinked PVP [32]. (**Figure (I.14)**) illustrates the specific properties of PVP.

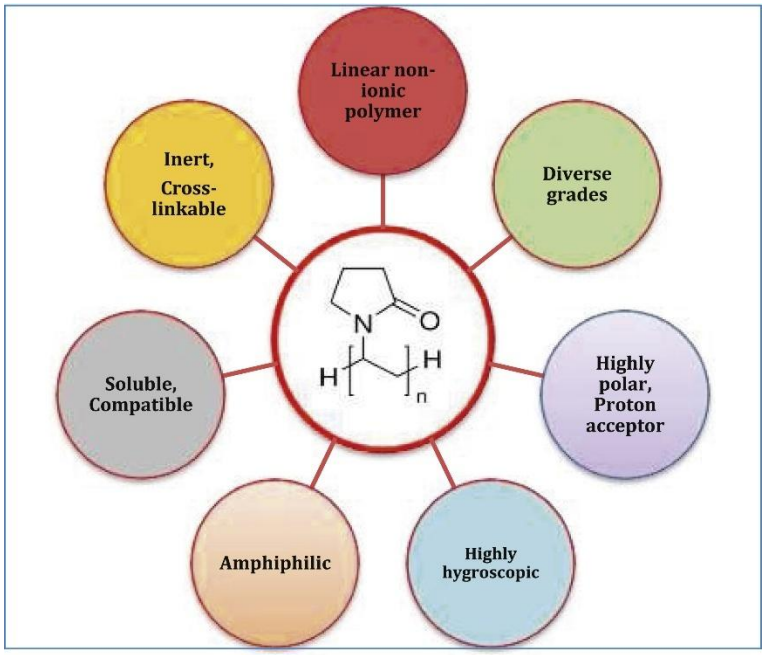

Figure (I.14): *Specific properties of PVP* [33].

I.4.1. Preparation of PVP:

PVP is synthesized using the Reppe Acetylene process, pioneered by BASF. The Reppe process starts with the manufacture of a monomer, N-vinylpyrrolidone, which is then polymerized to produce the end product, PVP [32].

I.4.1.1. Synthesis of monomer, N-vinylpyrrolidone:

As illustrated in **Figure (I.15)**, the Reppe method comprises a five-step reaction that starts with acetylene to produce N-vinylpyrrolidone.

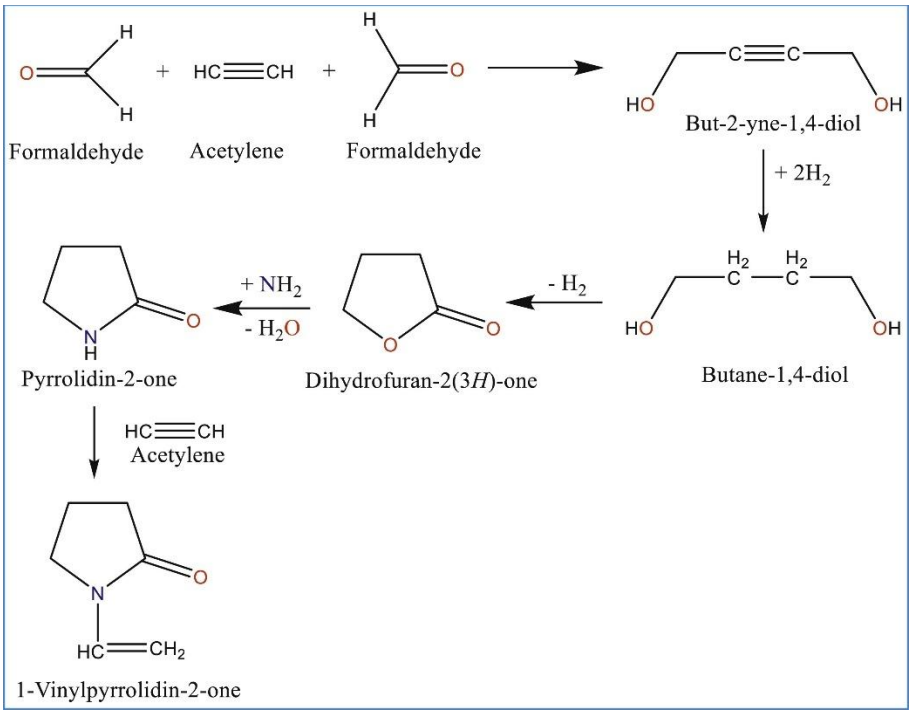

Figure (I.15): *Synthesis of N-vinylpyrrolidone by following Reppe chemistry* [33].

I.4.1.2. Polymerization of monomer:

The monomer, N-vinylpyrrolidone, synthesized from the Reppe method is subsequently processed to produce PVP, as illustrated in (**Figure (I.16)**) PVP is classified into three forms based on the synthetic procedure: homopolymers (with varying molecular weights), copolymers, and cross-linked PVP.

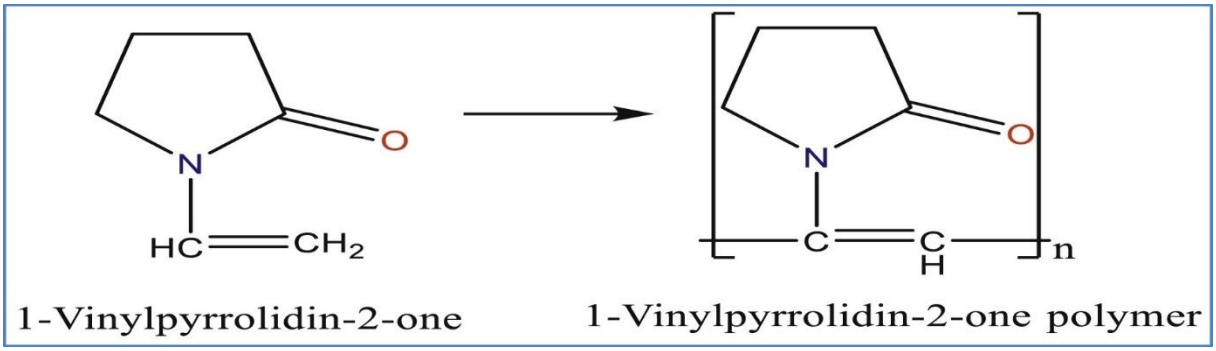

Figure (I.16): *Polymerization of N-vinylpyrrolidone* [33].

I.5. PVP-coated metallic nanoparticles:

Nanoparticles must be stable and trustworthy throughout time, with well-controlled and well-defined qualities, before they can be used for any purpose. Stability is one of the challenges that should be addressed more thoroughly, since aggregation can result in a full decrease or loss of nanoscale features. Numerous investigations have been undertaken, particularly on noble metal nanoparticles (gold, silver, etc.), as well as iron and zinc nanoparticles. To change the surface of nanoparticles and increase their characteristics, a variety of coating and stabilizing agents have been utilized, including surfactants (cetrimonium bromide) and polymers (polyvinylpyrrolidone) [34].

Concerns over the safety and long-term toxicity of nanoparticles in biological systems need to be addressed. Biocapping with aqueous plant extracts is an excellent technique to control the development of nanoparticles while minimizing toxicity. However, because surface modification of nanocrystals is required to create monodisperse nanoparticles, poly dispersion and purification from by-products is a hindrance to the use of this technology on an industrial scale (**Figure (I.17)**).

PVP, often called povidone or polyvidone, is a water-soluble polymer (C6H9NO). PVP is formed by polymerizing the monomer N-vinylpyrrolidone. It is a light, flaky, hygroscopic powder. It absorbs around 40% of water based on its mass. It has great moisturizing qualities. As a result, films create a compelling coating agent. PVP's unique physicochemical features, including as solubility in both water and organic solvents, biocompatibility, chemical stability, and non-toxicity, make it a promising biomaterial for a variety of important medical and non-medical applications. PVP is widely utilized in a variety of medicinal, cosmetic, and hair-care products. PVP is commonly used in the pharmaceutical industry to manufacture drugs as a common ingredient in tablets, granules, pellets, soft gelatine capsules, gels, hydrogels, films and coatings, nanofiber membranes and mats, powders, syrups, oral or injectable solutions, medical device coatings, contact lenses, and many other applications. PVP is a capping agent used in nanotechnology to address disadvantages of traditional nanoparticle manufacturing processes, including toxicity, size, and agglomeration. As a result, ecofriendly nano formulations are created utilizing PVP, which is more widely applicable. In various researches, PVP has been employed as a capping agent around metal nanoparticles such as Iron (Fe), silver (Ag), gold (Au), zinc (Zn), etc [35]. In this work, zinc

oxide particles were coated with PVP to improve stability and dispersion, resulting in increased surface area and the capacity to absorb contaminants.

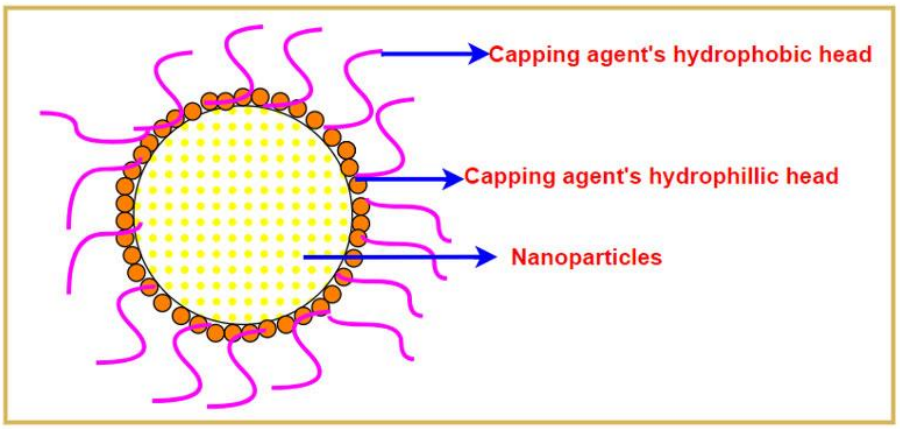

Figure (I.17): *Nanoparticles covalently bound with capping agents* [36].

I.6. Methods for Synthesizing Metal Oxide Nanoparticles:

MNP synthesis consists mostly of two approaches: the top-down technique, also known as the dispersion method, and the bottom-up strategy, or condensation method. In the top-down technique, nanoparticles are created using the size reduction process, which breaks down bulk materials into tiny components. This may be done by using high-intensity ultrasonic generators that operate at frequencies of roughly 1,200,000 rpm. Another way for dispersion is to create an electric arc within the liquid. The tremendous heat created by the electric arc causes metal to diffuse as vapor from the electrode, which then condenses to form MNPs. Bottom-up assembly creates nanostructures atom by atom or particle by particle. This may be achieved with a high degree of supersaturation followed by nuclei development (**Figure (I.18)**).

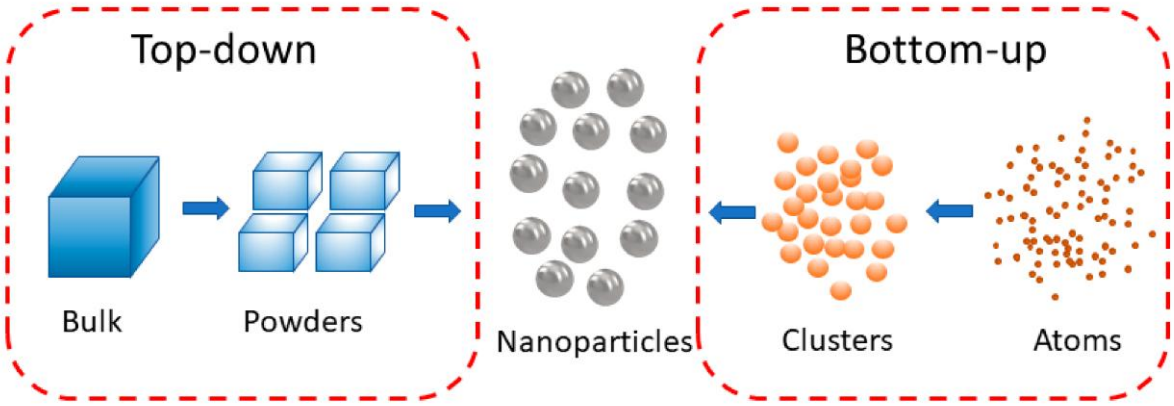

Figure (I.18): *Scheme of top-down and bottom-up synthesis of nanoparticles (NPs)*[37].

Considering these two approaches, various scientists have reported a variety of chemical and physical methods for producing MPs, such as chemical reduction, microemulsion, thermal decomposition, Sono chemical, polyol method, microwave-assisted method, laser ablation, sputtering deposition, lithography, pulsed electrochemical etching, vapor deposition, and sol-gel [38](**Figure (I.19)**).

In this study, we will provide a brief explanation of some of these method

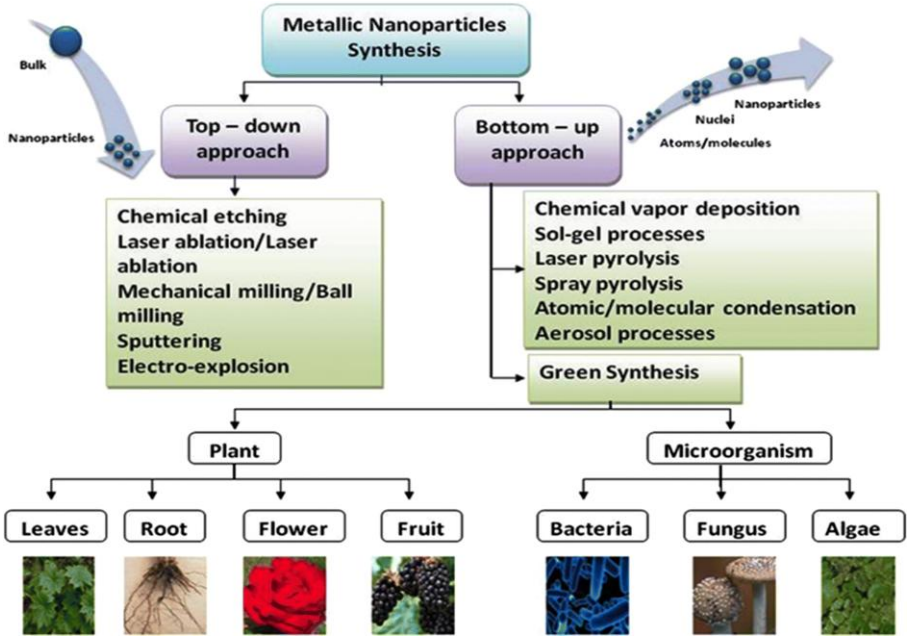

Figure (I.19): *Different synthesis approaches available for the preparation of metal nanoparticles* [39].

I.6.1. Synthesis of Nanoparticles by Co-precipitation Process:

Chemical coprecipitation is a common method for producing metal oxide nanoparticles due to its simplicity, low cost, and ability to generate homogenous and highly crystalline nanoparticles. This approach inhibits nanoparticle aggregation by precipitating several metal ions from a solution by adjusting the pH and using a capping or stabilizing agent. Metal ions required for co-precipitation are given by dissolved metal salts in water, such as chlorides, nitrates, and sulfates. Sodium hydroxide (NaOH) and ammonia (NH_3), two strong bases, are commonly utilized as precipitating agents to produce metal hydroxides. When these metal hydroxides are heated or aged, they degrade into metal oxide nanoparticles. The co precipitation process produces nanoparticles with excellent purity and uniform size distribution, and allows for adjusting the composition of

mixed metal oxides by changing the ratio of metal precursors. This method is ideal for industrial settings due to its large-scale synthesis capabilities. However, challenges include homogeneity and managing nanoparticle size and shape. When optimized, it can yield nanoparticles suitable for various applications, including sensors, environmental remediation, and catalysis.

I.6.2. Synthesis of Nanoparticles by Sol-Gel Process:

The technique involves using a suitable chemical solution as a precursor. Metal oxide and chloride are typical solgel technique precursors. Metal oxides and chlorides are the most often used sol-gel precursors. Sol-gel synthesis is a popular method for synthesizing nanomaterials, combining the terms 'gel' and ‘sol'. The process involves a sol-gel forming a three-sided channel in the solvents, which is then frozen and deformed into solids through liquid removal or evaporation. This method produces high-quality materials with homogeneity and purity at lower temperatures than conventional procedures. However, the main limitation is the lengthy processing time [27] (**Figure (I.20)**).

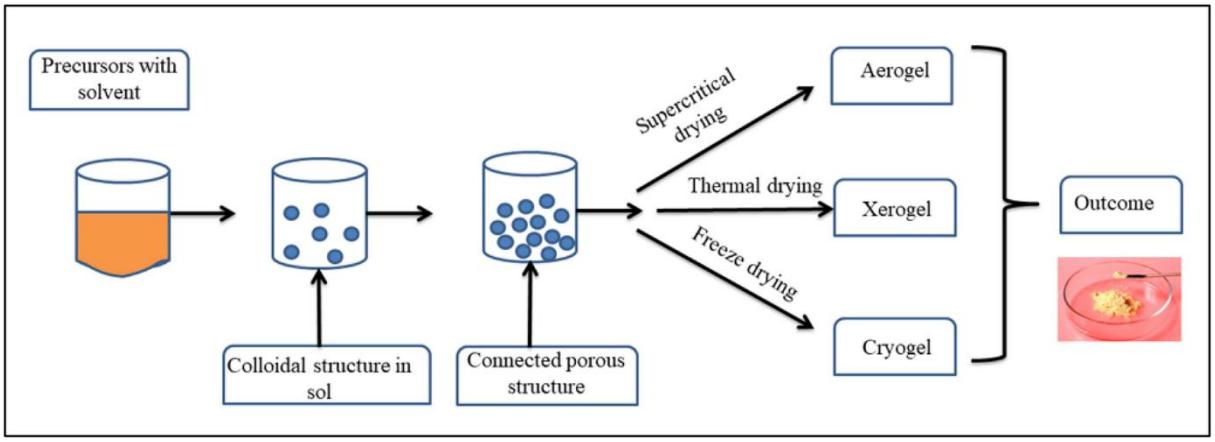

Figure (I.20): *Sol-gel method- step-by-step process for nanoparticle synthesis* [40].

I.6.3. Synthesis of Nanoparticles by Hydrothermal Process:

Hydrothermal synthesis is a process of crystal growth under high temperature and pressure water conditions, resulting from substances insoluble in ordinary conditions. The ionic product (Kw) has a maximum value of 250-300 °C, so hydrothermal synthesis is usually conducted below 300 °C. The critical temperature and pressure of water are 374 °C and 22.1 MPa, respectively. Under supercritical conditions, solvent properties like dielectric constant and solubility significantly change. The dielectric constant of water decreases with temperature and pressure, and under supercritical conditions, it contributes significantly to reaction rates, enhancing reaction rates

and causing large supersaturation. Supercritical water synthesis improves the reaction rate of multi metal oxide compounds by over 103 times compared to conventional hydrothermal conditions. This is due to the low dielectric constant (<10) and high crystallinity of the products. Metal oxide particle size is determined by its hydrolysis rate and solubility. Hydrothermal temperature and pressure parameters in subcritical and supercritical water may be adjusted to influence the solvent field during particle nucleation and crystallization. Hydrothermal techniques for preparing tiny metal oxide particles in subcritical and supercritical water were developed utilizing batch reaction and flow reaction systems [41].

I.6.4. Synthesis of Nanoparticles by Green Chemistry:

Green chemistry for sustainable development has been widely investigated during the last 15 years. The three most crucial requirements for nanomaterial production are the use of an environmentally benign solvent, a suitable reducing agent, and a good stabilizing agent. Chemical procedures can be costly and have environmental dangers. However, biosynthetic approaches provide a safer and more environmentally friendly alternative. Green synthesis is necessary to avoid the formation of undesirable or dangerous byproducts by developing dependable, sustainable, and environmentally friendly synthesis techniques. This objective requires the utilization of optimal solvent systems as well as natural resources (such as organic systems). The green production of metallic nanoparticles has been used to accommodate a variety of biological components. Plant extracts are a straightforward green approach for producing metal/metal oxide nanoparticles on a large scale, unlike bacteria or fungi-mediated synthesis. These materials are collectively known as "biogenic nanoparticles."

Green synthesis techniques based on biological precursors are influenced by a variety of reaction parameters, including solvent, temperature, pressure, and pH (acidic, basic, or neutral). Plant biodiversity has been widely considered for the synthesis of metal/metal oxide nanoparticles due to the abundance of effective phytochemicals in various plant extracts, particularly leaves, such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. These components are able to convert metal salts into metal nanoparticles. Nanomaterials have been studied for several applications, including biomedical diagnostics, antimicrobials, catalysis, molecular sensing, optical imaging, and biological system labeling [39].

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CHAPTER II
Synthesis and Characterization

II.1. Synthesis of Metallic Oxide Nanoparticles by Co-precipitation

The co-precipitation method is a widely used technique for synthesizing metal oxide nanoparticles due to its simplicity, cost-effectiveness, and ability to produce nanoparticles on a large scale. This method involves the precipitation of metal ions from the solution, resulting in the formation of nanoparticles with controlled size and shape. This is achieved by mixing an NaOH solution with the corresponding metal solution to form a metal hydroxide or oxide precipitate, which is then washed, dried, and calcined. The co-precipitation method involves the supersaturation of metal ion solutions, leading to precipitation. Several prior research have demonstrated that this technique's high production capacity allows for the creation of metal oxide particles such as ZnO, CuO, MgO, Fe_3O_4, and others [1].

In this work, ZnO nanoparticles were produced utilizing the co-precipitation approach, which proved to be efficient in creating high-quality nanoparticles in terms of form and size. Additionally, these particles were modified by covering them with PVP to improve their characteristics.

II.2. Materials and Methods:

To synthesize zinc oxide nanoparticles, zinc acetate (Zn $(CH_3CO_2)_2$) was used as a precursor and sodium hydroxide (NaOH) as a pH controller and precipitating agent. The key step in this work is the introduction of polyvinylpyrrolidone (PVP) with a specific molecular weigh(~40,000 g/mol) as a coating material. These materials were used as solutions using distilled water.

II.2.1. Synthesis of Zinc Oxide Nanoparticles by Co-precipitation Method:

To synthesize ZnO Nanoparticle by co-precipitation method, we prepare 900 mL of a 0.2 M Zinc acetate (Zn $(CH_3CO_2)_2$) solution and heat it to 75 °C with continuous stirring. We gradually introduce 2 M sodium hydroxide (NaOH) solution over 5 minutes, monitoring the reaction closely. We adjust the pH to 11 with the same NaOH solution, ensuring precise control during this step. We continue stirring the mixture at 75 °C for 2 hours, observing for a distinct color change that confirms the formation of the nanocomposite (**Figure (II.1)**). Once the reaction completes, we separate the precipitate by centrifuging at 3000 rpm for 5 minutes. We wash the collected material multiple times with distilled water to eliminate impurities effectively. We dry the purified precipitate in an oven at 100 °C for 18 hours. Following this, we transfer the dried material to a furnace and calcine it at 500 °C for 3 hours. This critical stage ensures the formation of ZnO NPs. We allow the product to cool to room temperature before proceeding with storage or further characterization [2], [3] (**Figure (II.2)**).

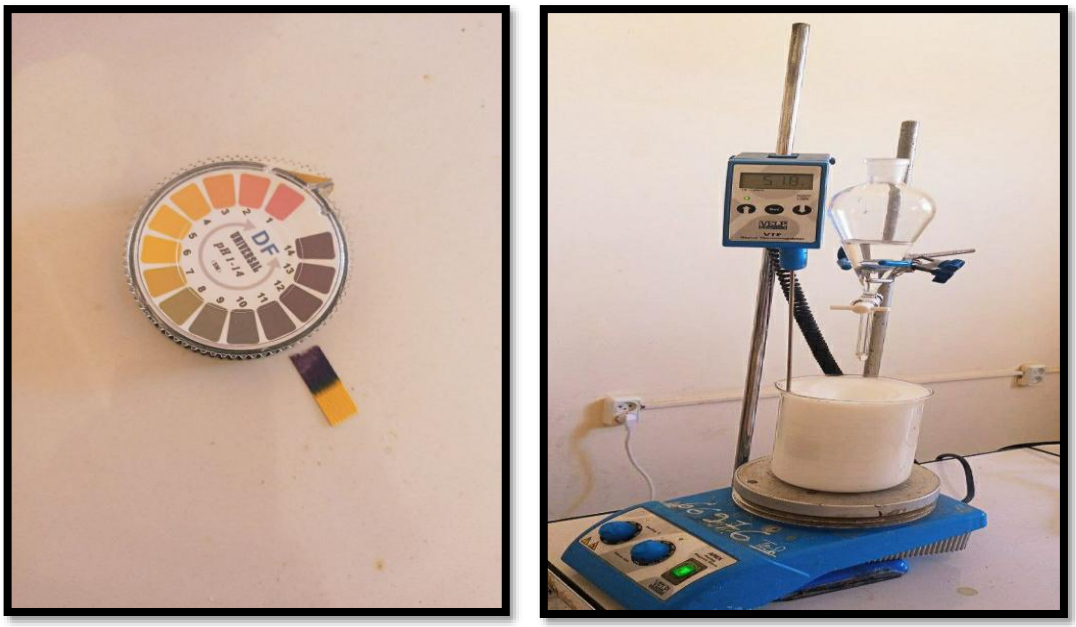

Figure (II.1): *Color Observation as an Indicator of Zinc Nanoparticle Formation at pH= 11*

II.2.2. Synthesis of PVP-coated Zinc Oxide Nanocomposite (NC):

Initially, a PVP and citric acid solution was prepared by dissolving 4 g of PVP (molecular weight ~40,000 g/mol) in 100 ml of distilled water under magnetic stirring at 40°C. This temperature was chosen to maintain the stability of the polymer and prevent its degradation. Subsequently, 2 g of citric acid was gradually added to the solution with continuous stirring until complete dissolution was achieved. In parallel, a ZnO suspension was prepared by suspending 6 g of ZnO nanoparticles in 100 ml of distilled water, followed by ultrasonic dispersion for 20 minutes to ensure a homogeneous distribution of the particles. In the next step, the PVP/citric acid solution was slowly added to the ZnO suspension under continuous stirring at 40°C to avoid any structural changes in the PVP. The stirring was maintained for 4 hours to ensure complete formation of the coating. Following this, the resulting ZnO@PVP NCs were dried in an oven at 40°C for 12 hours to ensure the stability of the coating without polymer degradation. Finally, the dried product was gently ground to obtain ZnO@PVP NCs with a homogeneous and stable coating layer. This synthesis method leverages the ability of PVP to form a stable coating around ZnO nanoparticles, enhancing their stability and potential applicability in heavy metal removal processes [4], [5] (**Figure (II.2)**).

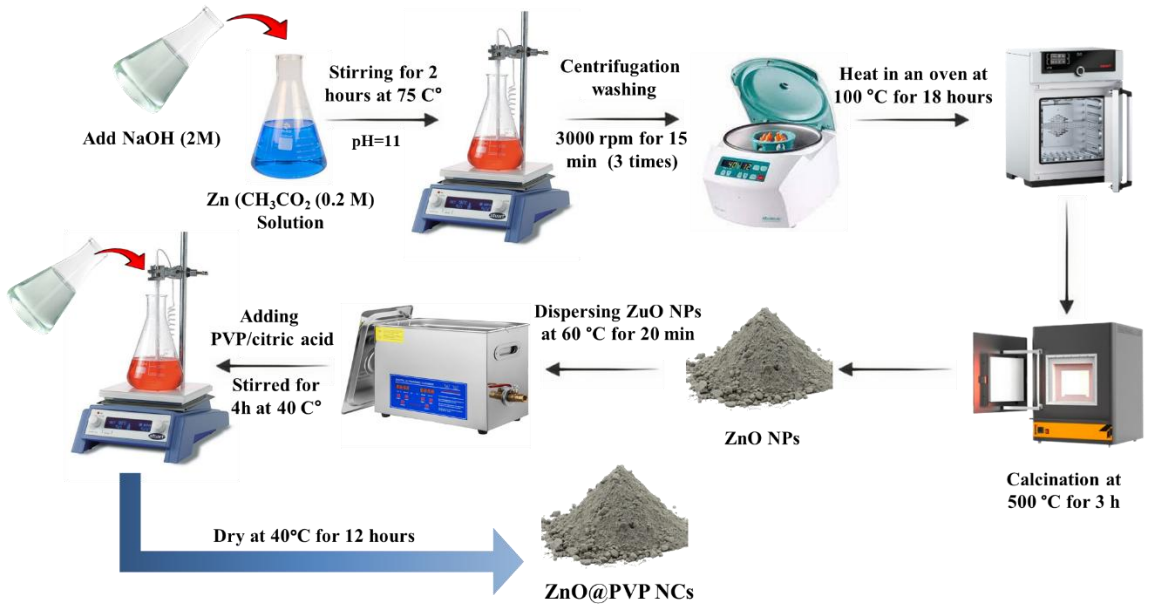

Figure (II.2): *Synthesis of ZnO Nanoparticles via Co-Precipitation Method with PVA Coating*

II.2.3. Characterization Techniques:

The development and uptake of nanomaterials for specific applications are largely dependent on their characterization. The distinct and innovative physico-chemical characteristics of nanomaterials led to the development of several characterization methods. As a result, nanoparticles are described in order to investigate a variety of physical and chemical characteristics, including composition, shape, surface area, optical properties, oxidation state, surface composition, and electrochemistry. A single approach should not be used for entire nanomaterial characterization since, often, many measurements are required to capture all relevant nanomaterial features [6]. In this study, three techniques were adopted to characterize the new nanocomposite: UV-Vis spectroscopy, Fourier-transform infrared spectroscopy, and X-ray diffraction. These will be briefly explained in this chapter.

II.2.3.1 Spectroscopy:

The study and identification of the amounts of spectra generated when materials interact with or emit electromagnetic radiation is the focus of the scientific field of spectroscopy. Because the electromagnetic waves are employed at different wavelengths, numerous kinds of interactions take place, including absorption, scattering, and reflection. Consequently, different spectra can be used to infer important information. Although spectroscopy may be done in a variety of ways, we will concentrate on the two approaches in this study [7].

II.2.3.1.1. UV-Visible Absorption Spectroscopy:

The employed quantitative analytical method known as ultraviolet visible (UV-vis) spectroscopy, absorption spectroscopy, or reflectance spectroscopy is frequently used to describe both nanomaterials. It measures how much a UV-vis light beam attenuates after passing through or reflecting off of a sample surface. The device used in UV-vis spectroscopy is called a UV-vis spectrophotometer, and it measures and contrasts the initial light intensity (I_0) before and after it interacts with a material (I). Transmittance is the ratio of I to I0; it is typically given as a percentage, %T. Equation (**Eq (II. 1)**) displays the absorbance (A) as a function of transmittance.

$$A = \log_{10}\left(\frac{\%T}{100}\right) \qquad \textbf{(II. 1)}$$

The spectroscopic technique operates on the principle of the Beer–Lambert law given as (**Eq (II. 2)**):

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon c l \qquad \textbf{(II. 2)}$$

where 'A' is the measured absorbance, I_0 is the initial light intensity before interaction with a sample at a given wavelength, I is the transmitted intensity, l is the path length through the sample, c is the concentration of the absorbing samples, and ε is a constant referred to as the "molar absorptivity" or "extinction coefficient."[7]

UV-vis spectroscopy analysis provides valuable information for scientists and practitioners, such as identifying chromophore functional groups, determining unknown compounds, determining material purity, and determining energy band gaps. Chromophores are materials with chemical bonds and functional groups that absorb ultraviolet and visible radiation.[7]

❖ **The principle of operation of the spectrophotometer:**

When enough energy-rich light strikes an atom, its electrons become excited and transition from a lower energy state to a higher one. The lowest unoccupied molecular orbit (LUMO) and the highest unoccupied molecular orbit (HOMO) are two classifications for an electron's energy state. The particular behavior of the material sample being studied is linked to the recognition of the evolution of bonds being generated. (**Figure (II.3) a**) shows the different bonds that form during a material's electronic transition. Depending on the type of bond created in the material, sigma (σ) is the strongest bond and pi (π) is the weakest. (**Figure (II.3) b**) illustrates a typical UV-vis absorption experiment for a substance in liquid. A monochromatic beam of light from a source is divided into two beams, one of which passes through the sample and the other via

the reference. The two beams are directed back to the detectors after transmission over the sample and reference, and they are compared to provide an output [7].

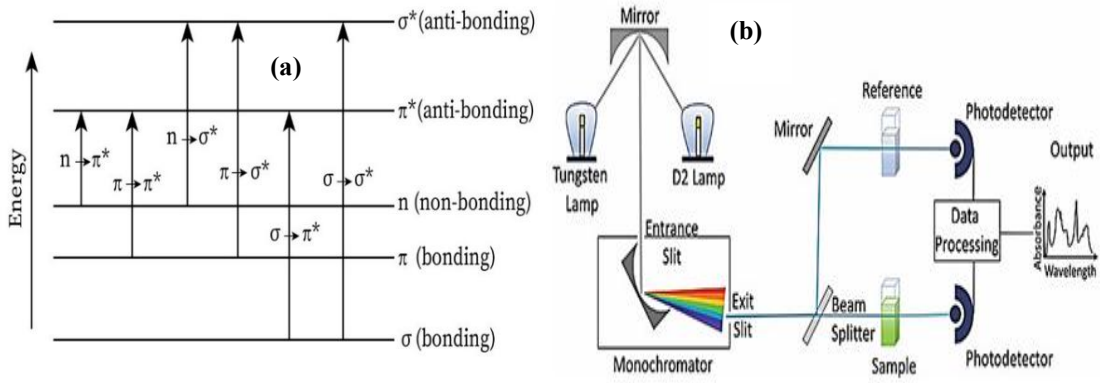

Figure (II.3): *(a) Shows the different bonds that form during a material's electronic transition; (b) Illustrates a typical UV-vis absorption experiment for a substance in liquid*

II.2.3.1.2 Fourier Transform Infrared (FTIR) Spectroscopy:

Is an analytical method based on infrared spectroscopy principles that has been used to analyze a variety of nanomaterials. It is a data measuring approach in which spectra are collected based on measurements of a radiative source's coherence made using time-domain or space-domain measurements of electromagnetic radiation. As a result, an FTIR spectrometer obtains spectral data throughout a wide spectral range**.**

The raw data is then turned into the actual spectrum using Fourier transformation based on Wiener-Khinchin theorem.

The FTIR spectrometer generates a spectrum by interfering with different frequencies of light. It consists of a light source, interferometer, sample chamber, and detector, among other things (**Figure (II.4)**). The light source generates electromagnetic radiation, which passes the sample through the interferometer and into the detector. The signal is subsequently sent to a computer, where it is converted into an intensity-versus-frequency spectrum using a mathematical technique known as the Fourier transform. FTIR is particularly effective for identifying compounds based on their chemical linkages (functional groups). The wavelength of light absorbed is a property of the chemical bond. Invariably, FTIR may be used to measure elements of an unknown mixture of solids, liquids, or gasses.

Because FTIR absorption is based on molecular vibration (which reflects a molecule's chemical property, such as an arrangement of nuclei and chemical bonds), it is used not only to identify molecules but also to examine their structures. Because molecular vibration is affected by the surrounding environment, the effect of the environment on the sample likewise influences FTIR. So FTIR may be used to determine the chemical bond (wave number range

from 900 to 1350 cm^{-1}), the functional group (1350-4000 cm^{-1}), and the functional group's surroundings [6-7].

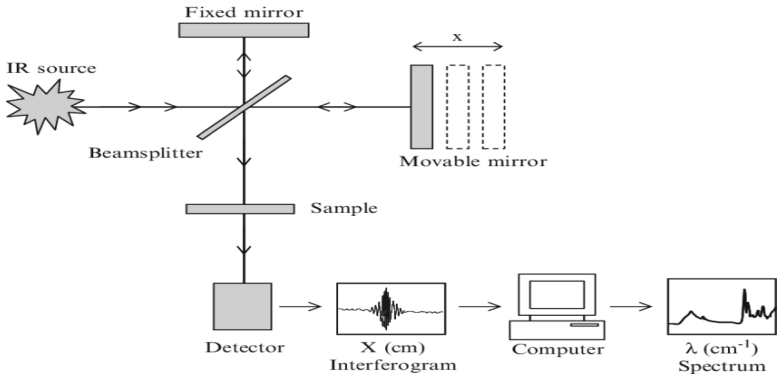

Figure (II.4): *Schematic diagram of Fourier-transform infrared spectrometer.*

II.2.3.2. X-ray Diffraction (XRD) :

In 1895, Rontgen accidently discovered X-rays in Crookes tube. After battling for 7 weeks, he discovered the nature of this new sort of radiation and dubbed it X Strahlen. He used X-rays for the first time to examine bones on a photographic plate. In 1897, it was discovered that when a metal mirror is irradiated, the intensity of the X-ray beam drops, and the intensity of the beam varies depending on the material. Thomson discovered secondary X-rays, which are the consequence of primary X-rays scattering from charged particles. Since its discovery, X-rays have been widely employed for studying the structural characteristics of materials ranging from crystalline solids to biological samples [8].

X-ray diffraction (XRD) is a strong method that is widely used to determine the crystal structure, grain size, nature of the crystalline phase, and lattice parameters of nanoparticles using X-ray radiation. These high-energy (100 eV-100 keV) radiations are produced when a focussed electron beam is accelerated over a high voltage field and bombards a stationary or spinning solid target. They penetrate deeply into a material and provide information on the structural arrangement of atoms and molecules. The lattice parameters of nanomaterials are calculated using the Scherrer equation and the broadening of the most intense peak from the XRD results. The diffraction angle and intensity of the peaks in the XRD pattern are then compared to the data available from the Joint Committee on Powder Diffraction Standards. X-rays predominantly interact with electrons in atoms, and during this interaction, some photons from the incident beam are reflected or diffracted away from their initial direction of travel (**Figure (II.5)**). The dispersed X-rays include information about the electron distribution in materials. If the atoms are grouped in a periodic pattern, as in crystals, the diffracted waves will

have sharp interference maxima (peaks) with the same symmetry as the distribution of atoms. Measuring the diffraction pattern allows one to determine the distribution of atoms in a substance. The peaks in an X-ray diffraction pattern correspond precisely to atomic distances [7].

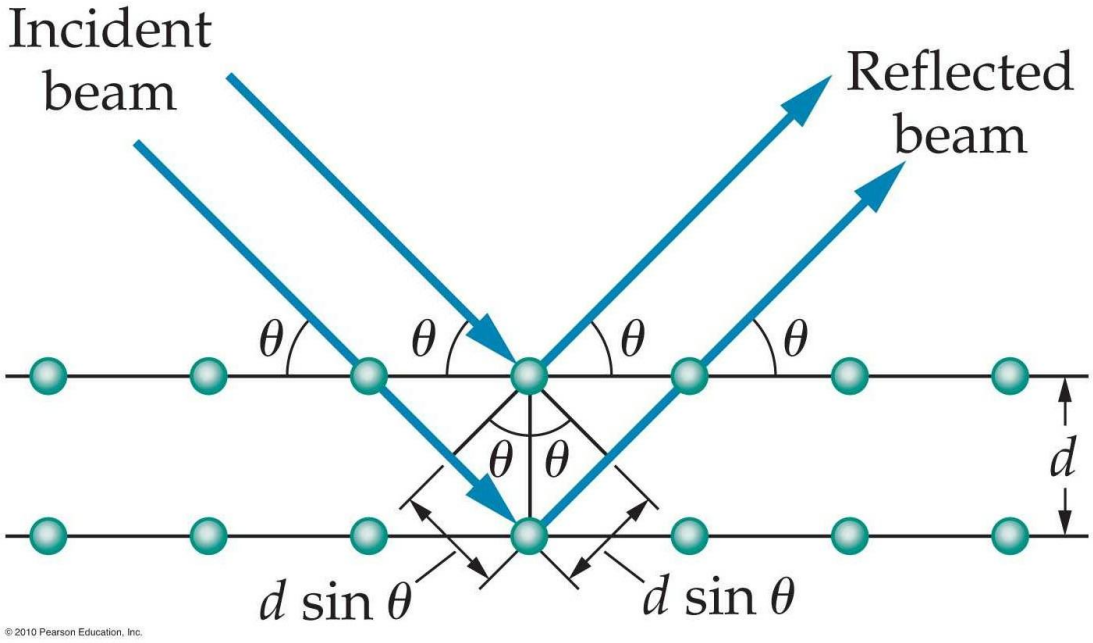

Figure (II.5): X-ray reflections from a crystal with the atoms in the two or more different plane

II.3. Results and Discussion:

II.3.1. Reduction of Ions and Involved Mechanism:

In this study, zinc oxide (ZnO) nanoparticles were synthesized via the co-precipitation method, using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as the zinc source and sodium hydroxide (NaOH) as both the precipitating agent and for pH adjustment. The synthesis process involved an acid-base reaction to form zinc hydroxide intermediates, followed by calcination at 500°C for 3 hours to produce ZnO nanoparticles. The concentrations of reagents and specific reaction conditions are detailed in the experimental section.

II.3.1.1. Mechanism:

When zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) is dissolved in water, it dissociates into zinc ions (Zn^{2+}) and acetate ions (CH_3COO^-) according to the following reaction:

$$Zn(CH_3COO)_2 \cdot 2H_2O \longrightarrow Zn^{2+} + 2CH_3COO^- + 2H_2O$$

During the synthesis, the addition of sodium hydroxide (NaOH) solution increases the pH to 11, promoting the reaction between Zn^{2+} ions and hydroxide ions (OH^-) to form zinc hydroxide ($Zn(OH)_2$), an insoluble white precipitate, as shown below:

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

❖ **Calcination:**

Calcination is a thermal treatment process involving the heating of solid materials at high temperatures (typically 300–600°C) to induce physical or chemical changes, such as dehydration or phase transformation. In this study, the zinc hydroxide ($Zn(OH)_2$) precipitate was ground and calcined at 500°C for 3 hours to produce zinc oxide (ZnO) nanoparticles, as described by the following reaction:

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

Calcination is a critical step in this synthesis, as it removes the hydroxyl groups (OH^-) from ($Zn(OH)_2$) , facilitating the formation of the crystalline ZnO lattice with oxygen in the form of O^{2-}.

This process also controls the crystallization, particle size, and morphology of the resulting ZnO nanoparticles

II.3.1.2. The effect of PVP on the surface of ZnO and its performance in reducing heavy metal ions:

The encapsulation procedure in this study employing (PVP) would change the surface characteristics of ZnO nanoparticles, affecting the interaction mechanism with metal ions in contaminated water via adsorption or reduction. The function of this encapsulation is:

- Coating ZnO NP with PVP alters its electrical and chemical properties.
- PVP contains active functional groups such as C=O and N، which help to bind metal ions in water and promote their reduction.
- PVP prevents the aggregation and clustering of particles، providing a larger active surface area and improving electronic properties that contribute to the binding of electrons to metal ions.

II.3.2. Characterization of PVP-coated Zinc Oxide Nanocomposites:

In this work, three approaches were applied to characterize the novel compound ZnO@PVP NCs. The optical characteristics of the compound were determined using ultraviolet-visible spectroscopy, functional groups and molecular interactions were elucidated using Fourier-transform infrared spectroscopy, and the structure was revealed using X-ray diffraction.

II.3.2.1. Optical Characterization:

The spectroscopic study of ultraviolet and visible rays for (ZnO NPs) and (ZnO@PVP NCs) yielded the following findings.

II.3.2.1.1. UV-Visible Absorption Spectrometer:

The UV-Visible spectroscopy results provide significant insights into the optical properties of ZnO@PVP nanocomposites (NCs) (**Figure (II.6)**). The absorption spectrum of PVP exhibits a peak at 205 nm with minimal absorption across the visible range, while ZnO nanoparticles (NPs) show a primary absorption peak at 311 nm (**Figure (II.6) a**). In contrast, ZnO@PVP NCs display two distinct absorption features: one at 311 nm, consistent with bare ZnO NPs, and a broader peak at 361 nm, indicative of the influence of the PVP coating. These absorption characteristics highlight the enhanced UV-visible light absorption of the nanocomposite, attributed to the interaction between ZnO and PVP components [9], [10].

Additionally, the band gap energy, determined from the Tauc plot, was found to be 1.94 eV for ZnO NPs and reduced to 1.81 eV for ZnO@PVP NCs (**Figure (II.6) b**). This lower band gap value reflects the modified electronic structure of the nanocomposite, suggesting improved light absorption in the UV-visible region, which is advantageous for applications in adsorption and photocatalysis. The reduced band gap energy indicates enhanced charge carrier mobility, positioning ZnO@PVP NCs as a promising material for environmental remediation and optoelectronic applications [11], [12].

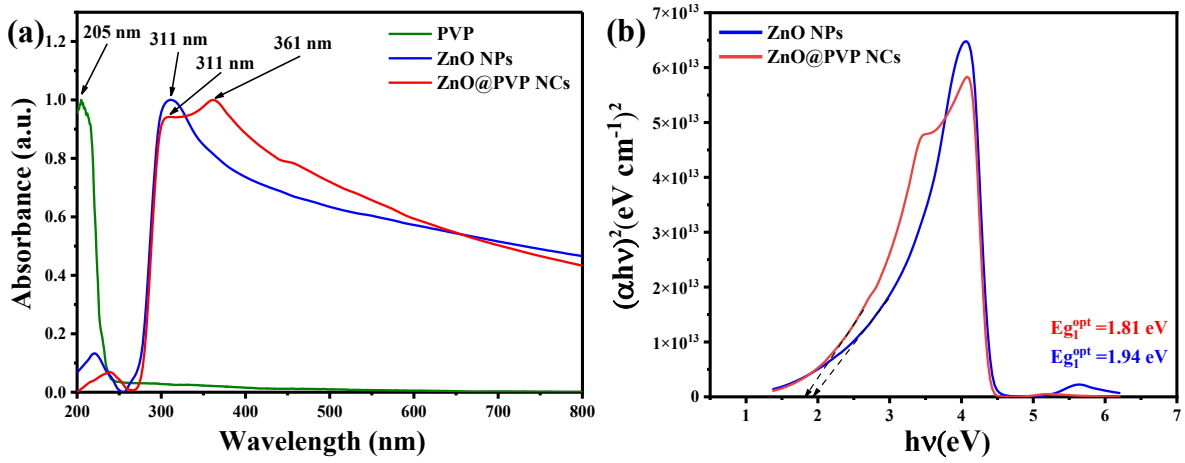

Figure (II.6): *Optical properties of ZnO@PVP nanocomposites (NCs): (a) UV-vis spectra; (b) Direct optical band gap energy*

II.3.2.1.2. Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared (FTIR) spectroscopy was employed to elucidate the functional groups and intermolecular interactions within ZnO@PVP nanocomposites (NCs), as depicted in (**Figure (II.7)**). This analysis offers critical insights into the chemical composition and structural stability of the synthesized materials, corroborating their successful integration.

The FTIR spectrum of pure polyvinylpyrrolidone (PVP) reveals a broad absorption band centered at approximately 3400 cm^{-1}, attributed to O-H stretching vibrations from hydroxyl groups, consistent with the presence of adsorbed moisture or inherent hydroxyl functionalities, as widely reported for PVP [12-13]. Peaks at 2950 cm^{-1} and 1650 cm^{-1} correspond to C-H and C=O stretching vibrations of the pyrrolidone ring, respectively, while bands at 1425 cm^{-1} and 1277 cm^{-1} arise from C-H and C-N stretching modes. A low-frequency peak at 572 cm^{-1} is assigned to N-C=O bending, aligning with established vibrational signatures of PVP [14-15]. For ZnO nanoparticles (NPs), characteristic peaks are observed at 1348 cm^{-1}, likely due to adsorbed carbonate species on the ZnO surface, a phenomenon noted in prior studies, alongside peaks at 832 cm^{-1} and 406 cm^{-1}, representing ZnO lattice vibrations and Zn-O stretching, respectively, which are hallmark features of ZnO nanomaterials [16-17].

The ZnO@PVP NCs spectrum integrates features from both constituents: a diminished O-H stretching band at 3373 cm^{-1}, suggesting reduced hydroxyl exposure due to ZnO-PVP interactions, and a persistent C=O peak at 1650 cm^{-1} from PVP. A slight shift from 1348 cm^{-1} (ZnO) to 1360 cm^{-1} in the composite indicates potential coordination or surface modification, consistent with polymer-metal oxide interactions reported in the literature [18-19]. Peaks at 830 cm^{-1} and 406 cm^{-1} mirror those of bare ZnO, confirming the retention of its core structure.

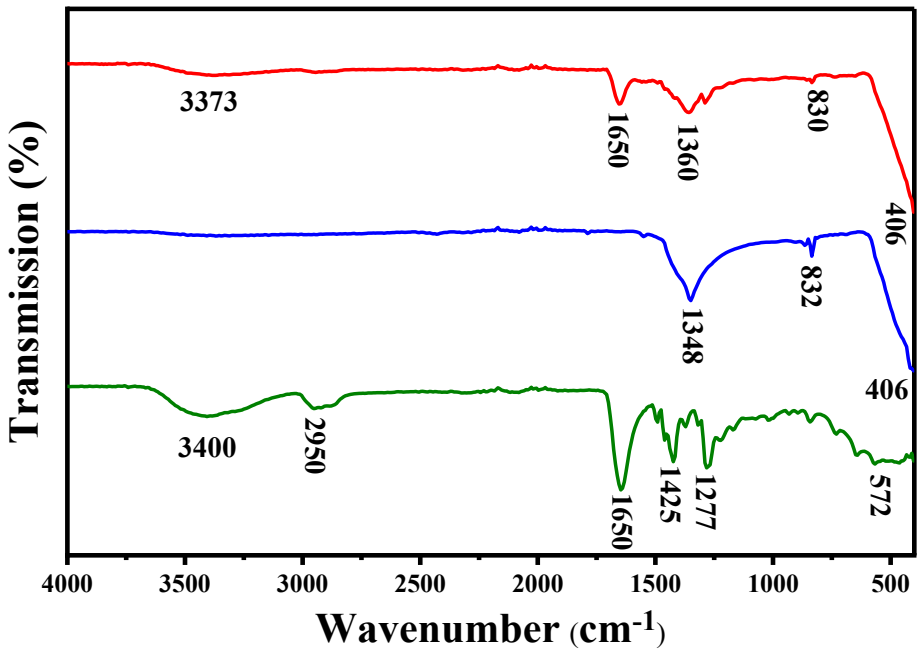

Figure (II.7): FTIR spectra of: PVP, ZnO NPs and ZnO@PVP NCs

II.3.2.2. Structural and Morphological Properties:

We previously conducted a calcination technique to investigate the fine structure and surface morphology of ZnO particles. In this investigation, X-ray diffraction was used to determine the structure of the novel nanocomposite ZnO@PVP NCs.

II.3.2.2.1. X-ray Diffraction (XRD) :

The structural properties of ZnO@PVP nanocomposites (NCs) were systematically characterized using X-ray diffraction (XRD) techniques. The XRD pattern, presented in (**Figure (II.8)**), reveals several distinct peaks characteristic of the ZnO@PVP NCs and their constituents. For ZnO nanoparticles (NPs), Bragg's reflection peaks are observed at 2θ values of 31.85°, 34.55°, 36.36°, 47.69°, 56.75°, 63.09°, 66.56°, 68.16°, 69.29°, 72.88°, and 77.21°, corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystal planes, respectively. These findings align with the Joint Committee on Powder Diffraction Standards (JCPDS Card N°. 01-079-0205), confirming a hexagonal wurtzite crystal structure with a space group of P63mc (space group number 186), lattice parameters a = b = 3.2417 Å, c = 5.1876 Å, and a calculated density of 5.72 g/cm³. The strongest peak at 36.36° (101) plane indicates high crystallinity with sharp, well-defined peaks [20-21].

For ZnO@PVP NCs, the XRD pattern retains all characteristic ZnO peaks at identical 2θ positions, affirming the preservation of the ZnO wurtzite structure. Additional peaks, marked with arrows (♠), appear at 2θ values of 11.56° and 21.64°, attributed to the amorphous PVP

phase, consistent with literature reports on PVP-containing composites [22-23]. The crystallite size (D_{XRD}) was calculated using the Debye-Scherrer equation (**Eq (II. 3)**) [25]:

$$D_{XRD} = \frac{K\lambda}{\beta \cos\theta} \qquad \textbf{(II. 3)}$$

Where D_{XRD} is the crystallite size (nm), K is the shape factor (0.9), λ is the Cu Kα wavelength (1.5406 Å), β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle. Using prominent ZnO peaks (e.g., 31.85°, 34.55°, 36.36°), the crystallite size was estimated at 22.84 ± 3.49 nm for ZnO NPs and 26.37 ± 2.90 nm for ZnO@PVP NCs, indicating a slight increase in size due to PVP coating.

Comparative analysis reveals that the incorporation of PVP does not alter the ZnO crystal structure or its crystallinity, though it introduces minor amorphous contributions from PVP. The XRD analysis confirms the successful synthesis of ZnO@PVP NCs, with the preserved hexagonal wurtzite structure and high crystallinity of ZnO, supporting their suitability for applications requiring robust nanostructured adsorbents [25-26].

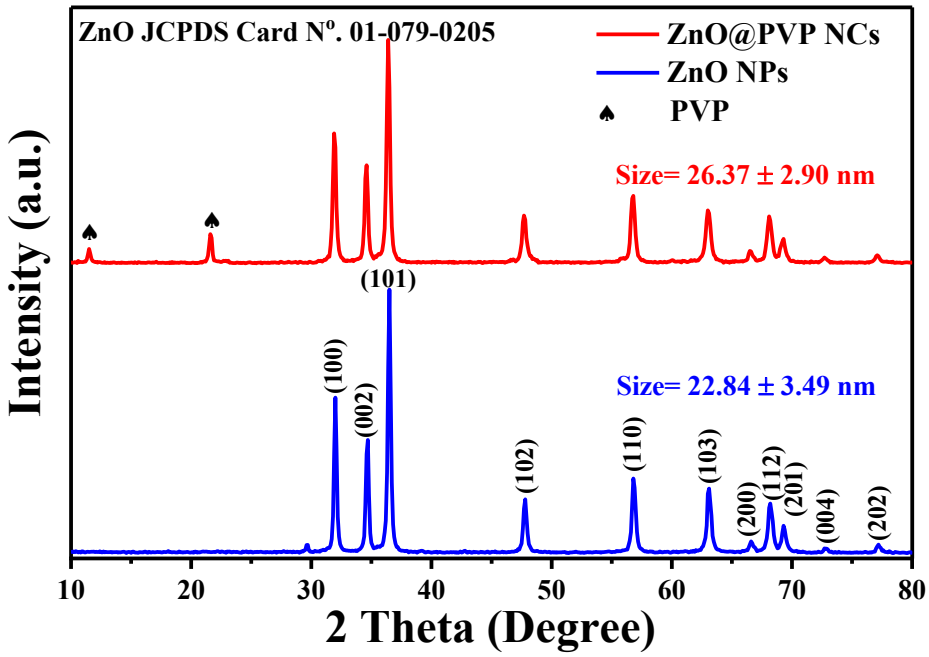

Figure (II.8): *X-ray diffraction patterns of ZnO NPs and ZnO@PVP NCs*

II.4. Conclusion:

This study successfully demonstrated the synthesis of polyvinylpyrrolidone (PVP)-coated zinc oxide (ZnO) nanoparticles via the co-precipitation method, with comprehensive characterization revealing significant enhancements in their properties. The incorporation of PVP as a coating material markedly improved the optical properties of ZnO nanoparticles, as evidenced by UV-Vis spectroscopy, which showed a characteristic absorption peak at 361 nm and a reduced bandgap from 1.94 eV to 1.81 eV. This reduction suggests enhanced charge carrier dynamics, positioning ZnO@PVP as a promising material for photocatalytic applications. FTIR spectroscopy provided evidence of strong chemical interactions between the ZnO core and PVP coating, indicated by shifts in vibrational bands of O H and C O functional groups, which contribute to the stability and functionality of the nanocomposite. XRD analysis confirmed that the hexagonal wurtzite structure of ZnO was preserved, indicating that the PVP coating does not disrupt the crystalline integrity of the nanoparticles. These findings highlight the effectiveness of PVP coating in tailoring the physicochemical properties of ZnO nanoparticles, offering potential for advanced applications in environmental remediation, particularly in the photocatalytic degradation of pollutants. Future research could explore optimization of synthesis parameters, such as PVP concentration and calcination conditions, to further enhance photocatalytic efficiency and evaluate the performance of ZnO@PVP in real-world environmental applications.

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CHAPTER III
Study of Efficient Heavy Metals Removal

III.1. Heavy Metals in Industrial Petroleum Wastewater:

Generally speaking, a metal is classified as heavy if its density is greater than 5 g per cubic centimeter. Although there are many elements in this category, the ones in **Table (III.1)** are significant in the context of the environment. Despite being a semi-metal, arsenic is typically considered a dangerous heavy metal. Reduced growth and development, cancer, organ damage, nervous system damage, and in severe cases, death, are just a few of the major health impacts that heavy metals can bring. Autoimmunity, a condition in which an individual's immune system targets its own cells, can also develop as a result of exposure to certain metals, including lead and mercury. Diseases of the kidneys, circulatory system, neurological system, and fetal brain can result from this, as well as joint conditions like rheumatoid arthritis. Higher concentrations of heavy metals can harm the brain permanently. Given that they eat more food per body weight than adults, children may be exposed to higher levels of metals through their diet. The purpose of wastewater laws was to reduce the exposure of humans and the environment to dangerous substances. This includes restrictions on the kinds and amounts of heavy metals that can be found in wastewater that is released. **Table (III.1)** provides a summary of the MCL criteria set by the USEPA for those heavy metals [1] .

Table (III.1): *Toxicities and Maximum Contaminant Levels (MCL) of Heavy Metals in Water*

Heavy Metal	**Toxicities**	**MCL (mg/L)**
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorders, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson’s disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs, increased thirst	0.80
Lead	Damage to fetal brain, diseases of kidneys, circulatory system, nervous system	0.006
Mercury	Rheumatoid arthritis, diseases of kidneys, circulatory system, nervous system	0.00003

III.1.1. Sources and Types of Heavy Metals:

III.1.1.1. Sources of heavy metals:

Both natural and man-made processes can release heavy metals, which can then find their way into the soil, water, air, and their interface (**Figure (III.1)**) [2].

III.1.1.1.1. Natural processes:

Various natural sources of heavy metals have been documented by numerous investigations. Natural releases of heavy metals take place under specific environmental circumstances (**Figure (III.2)**). Volcanic eruptions, sea salt sprays, forest fires, rock weathering, biogenic sources, and wind-borne soil particles are examples of these emissions. Metals may be released from their endemic spheres into various environmental compartments as a result of natural weathering processes. Hydroxides, oxides, sulphides, sulphates, phosphates, silicates, and organic compounds are all forms of heavy metals.

Lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn), and copper (Cu) are the most prevalent heavy metals. Even though the aforementioned heavy metals are present in small amounts, they nevertheless pose a major threat to human and other mammal health [2].

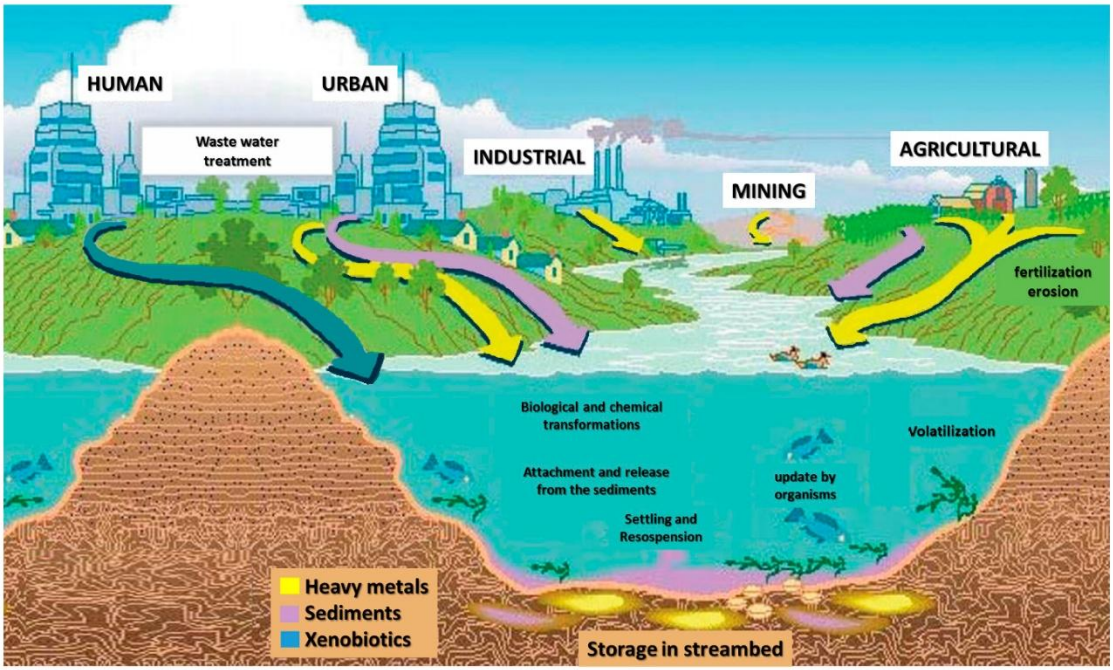

Figure (III.1): Sources and sinks of heavy metals [3].

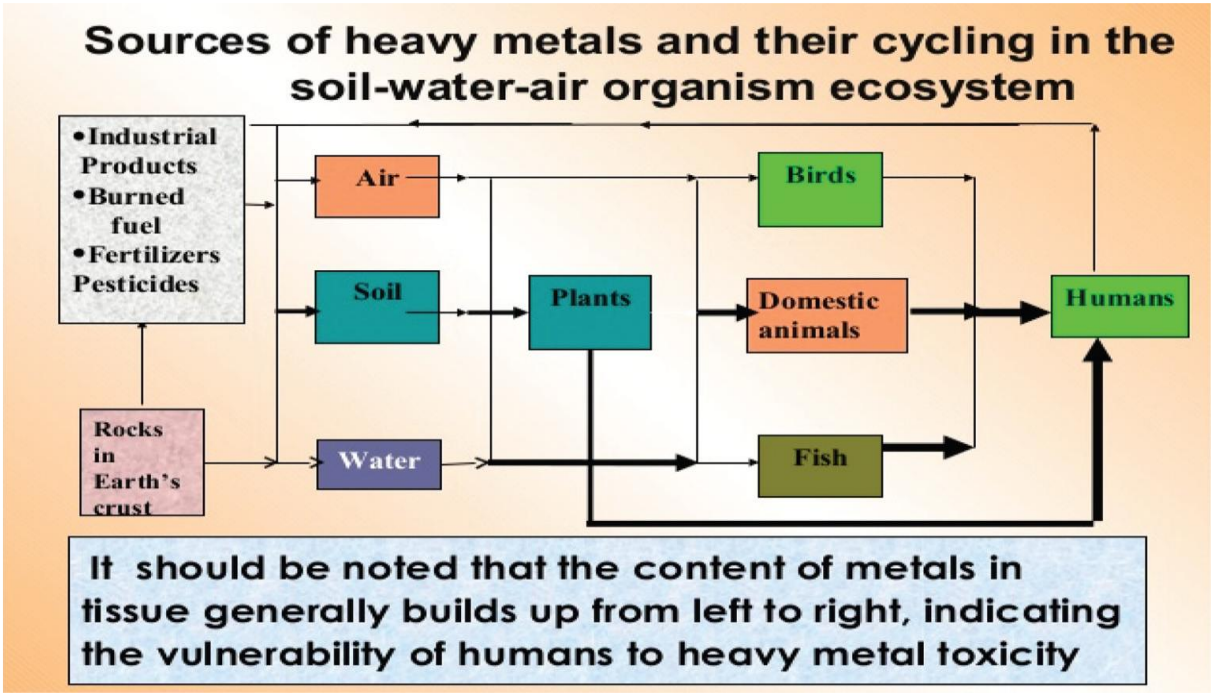

Figure (III.2): *Sources of heavy metals and their cycle in the environment* [4].

III.1.1.1.2. Anthropogenic processes:

Pollutants are also released into many environmental compartments by industries, agriculture, wastewater, mining and metallurgical operations, and runoffs. It has been observed that anthropogenic processes of heavy metals surpass the natural fluxes of some metals. The majority of the metals that are naturally released in wind-blown dusts come from industrial locations. The release of lead from vehicle exhaust, arsenic, copper, and zinc from smelting, arsenic from insecticides, and nickel, vanadium, mercury, selenium, and tin from burning fossil fuels are some significant anthropogenic sources that contribute to the environmental contamination of heavy metals. Because of the daily production of commodities to satisfy the desires of the huge population, it has been discovered that human activities are the primary cause of environmental pollution [2].

III.1.1.2. Industrial wastewater sources:

Heavy metal-containing industrial effluent streams are produced by several industries. Numerous applications produce large amounts of wastewater containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) that are produced by electroplating and metal surface treatment operations. These consist of milling, etching, conversion coating, anodizing-cleaning, electroplating, and electroless depositions. Manufacturing of printed circuit boards (PCBs) is another important source of heavy metal waste. The most common resistant over plates are made of solder plates made of tin, lead, and

nickel. Inorganic pigment manufacturing, which produces pigments containing chromium compounds and cadmium sulfide; petroleum refining, which produces conversion catalysts contaminated with nickel, vanadium, and chromium; photovoltaic operations, which produce film with high concentrations of silver and ferrocyanide; and the wood processing industry, which produces wastes containing arsenic from chromated copper-arsenate wood treatment. According to some studies, all these sources produce a large amount of wastewater, sludge, and sediment that fall under the category of hazardous waste and require intensive treatment [1].

III.1.1.3. Types of Heavy Metals:

III.1.1.3.1. Mercury (Hg):

Mercury was well recognized in antiquity, and the Phoenicians traded cinnabar from Almaden, Spain. It was applied as a cosmetic and as a decorative pigment called vermillion. Like the silver mines, the mercury mines at Almaden were infamously unhealthy and operated by slaves or prisoners during the Roman era. Nearly all of these individuals would have contracted mercury sickness from breathing in mercury fumes from the mine's atmosphere. During the Middle Ages, manuscript illuminators applied gold to their work using mercury. After creating and painting a mixture of gold and mercury on vellum or parchment, the mercury was allowed to evaporate—either with or without heat—leaving the gold in its place.

Later on, this extremely risky method was applied much more widely to apply gold adornment to small items like buttons or furniture; silver mirrors were also subjected to a similar procedure. Nearly everyone involved in this kind of labor may anticipate becoming poisoned by it, either by letting the mercury touch their skin or by breathing in mercury fumes. However, there was minimal mercury escape into the environment, and it was doubtful that anyone who did not work with it would have encountered it.

In contrast, occupational mercury poisoning is now uncommon (at least in developed nations), but endemics of environmental poisoning are not uncommon due to the use of mercurial fungicides to treat grain and the discharge of mercury from factories into rivers and lakes, where fish are the primary food source for the local population [5].

III.1.1.3.2. Cadmium (Cd):

Cadmium, which is basically a "modern" metal, was seldom ever used in ancient technologies save from the production of an exceptionally shiny, bright yellow bronze. However, it's probable that some environmental exposure happened to those who lived on cadmium-rich soils or who drank or irrigated with cadmium-rich water. Because cadmium is also present in some lead ores, exposure to cadmium may have happened in areas where these

ores were used. However, given that high body burdens, like those caused by occupational exposure, are necessary before detrimental effects on the kidneys and other two organs become evident, modern experience would indicate that none of these exposures would have been likely to be linked to significant health problems [5].

III.1.1.3.3. Lead (Pb):

Though it was initially prized not for its own sake but rather because it was the primary source of silver in the ancient world and the silver mines of antiquity were actually galena (lead sulfide) mines, lead has been utilized by humans in one form or another for at least 4,000 years. The most significant of these mines were located in Asia Minor, and some of their ores had more than 1.5% silver in them. Athens' prosperity was mostly reliant on mines like this one, particularly the one at Laurion.

Through the extremely risky technique of cupellation, silver was extracted from the ore. The procedure was very straightforward: the ore was melted, the lead oxide that developed on the molten metal's surface was then removed, and eventually, silver in various purity levels was left behind. Due to its high solubility in tissue fluids, lead oxide is a very hazardous form of the metal, and it is inconceivable that anyone working on this project could have avoided injury. In reality, it was far riskier than mining galena, which is comparatively non-toxic due to its near-insoluble nature.

The Roman water engineers utilized lead widely, and even though Vitruvius3 denounced this technique, it would only have been dangerous in places with soft or acidic water because only in these circumstances is the water plumbo-solvent. Food and drink adulteration, whether intentional or unintentional, was far more harmful. The addition of lead to wine to enhance its flavor and, thus, its marketability was the most dangerous of these. This practice persisted into relatively recent times, guaranteeing that a significant section of the populace was exposed to lead in one way or another and that lead poisoning was also prevalent [5].

III.1.1.3.4. Chromium (Cr):

Chromium is one of the heavy metals whose concentration keeps increasing due to industrial growth, especially the expansion of the chemical and tanning industries. Chromium is released into the environment by a variety of processes, including electroplating, leather tanning, wood preservation, pulp processing, steel manufacturing, and many more. The levels of nickel and chromium in the environment also vary widely. Serious concerns are raised by the increased use of these two metals in developing countries as well as their non-degradability.

Hexavalent chromium is extremely soluble in the human body and carcinogenic. This same hexavalent chromium is widely used in the metallurgies, refractory, chemical, and tannery industries, as is also well known [6].

III.1.1.3.5. Iron (Fe):

Iron is one of the heavy metals in the first row of transition metals. Fe^{3+} is the primary type observed, while Fe^{2+} is also identified. The porphyrin enzyme of respiration uses iron as a reducing and oxidizing agent (Vines and Rees).

Iron, the fourth most common element in the earth's crust, is found in seawater at about 3.5 parts per million. It responds really rapidly. Iron is by far the most prevalent and important transition metal (heavy metal) with a function in biological systems. Iron-containing proteins participate in the movement of electrons and oxygen, respectively. The function of other molecules is to transport and store iron. Humans and many other higher animals use ferritin and albumin as storing proteins [6].

III.1.1.3.6. Nickel (Ni):

When it comes to studying plants and soil, nickel is the most beneficial element. The development of marine microalgae seems to depend on nickel. Foods with very low nickel contents (e.g., 40.00 ug/g) can have negative effects on iron absorption, liver metabolism, and the activity of several enzymes. Around the world, soil has an average nickel concentration of 40.00 mg/g. The average daily dietary nickel intake, excluding the emission effect, was calculated to be 16,511 ug. The exposure pathway and the solubility of the nickel molecule dictate the toxicity of nickel. According to epidemiology research, occupational exposure to nickel (Ni) dust by inhalation can raise the risk of developing nasal and pulmonary cancer [6].

III.1.1.3.7. Copper (Cu):

The earth's crust contains the heavy metal copper, which is pliable, has a high melting point, and conducts heat well. Since the ninth century, civilizations have utilized it for a variety of purposes, including electrical wire, roofing, plumbing supplies, cookware, brake pads for automobiles, and agricultural products. Both natural and man-made processes, such as mining, the manufacturing of metal and electricity, the use of pesticides in agriculture, the processing of leather, and the manufacture of brake pads for automobiles, contribute to the environmental presence of copper. Anemia, liver and kidney damage, and inflammation of the stomach and intestines can all result from excessive copper exposure.

Hemolysis, cirrhosis, chronic anemia, and hepatotoxic and nephrotoxic effects can result from copper contamination in water systems. Because copper is toxic, non-biodegradable, and

readily accumulated in living things, it can cause serious illnesses and even death. The availability of the distribution system, pH, and hardness all affect the amount of copper in drinking water [7].

III.1.1.3.7. Zinc (Zn):

In the first row of transition metals on the periodic table, zinc is a heavy metal. Everywhere you look, you can find zinc, which has been proved to help plants and some rodents develop. In fruit trees, its lack results in mottled leaf disease. Mammalian enzymes like carbonic anhydrase contain zinc. It is necessary for the metabolism of proteins and seems to have some role in the synthesis of chlorophyll. Because zinc is a component of several enzymes and has a function in the synthesis of auxin, it is crucial for plant growth. Auxin is made from tryptophan, a chemical that requires zinc for production. Early in the 20th century, a number of crop diseases that are now known to be caused by zinc deficits were observed. Leaf chlorosis, primarily on veins and varying in color from white to light green, is one of the indications of zinc deficiency in all plants, according to a detailed analysis. When soluble or total phosphate levels in soils are excessively high, zinc deficiency is frequent. An early investigation on fluoride-deficient zinc in Tung's trees found that high soil phosphate levels were a significant role in lowering the amount of zinc that was available. Heavy metal toxicity, most frequently intestinal distress, can result from a comparatively low concentration of the element in the body [6].

III.1.1.3.8. Arsenic (As):

Arsenic is found in soil with an average concentration of 2–5 mg/kg8. The most significant natural source of AS is volcanic activity, which has the capacity to spew massive volumes of AS into the atmosphere.

Forest fires, soil or rock erosion, and other man-made causes are other sources of AS. The release of naturally occurring AS is accelerated and exacerbated by anthropogenic sources. There are around 320 AS-containing mineral species in nature. The most prevalent source of AS in nature is found in ores. Niccolite, realger, orpiment, lobaltile, arsenopyrite, and tennantites are the most significant ores that include AS. The most prevalent mineral that contains AS is arsenopyrite (FeAsS). The AS ions adsorb onto the Fe (III) and Mn (IV) oxide-hydroxide phases during the weathering of the AS material. Twelve the source of AS in natural water is the minerals that contain AS. The byproduct of dust and residues created during the smelting of copper and gold is arsenic trioxide. Arsenic is released into the environment directly by anthropogenic industrial sources [8].

III.1.2. Environmental Impact of Heavy Metals:

III.1.2.1 Toxic effect of some heavy metals:

Thirty of the 92 naturally occurring elements are known to have the potential to be hazardous to humans. Both natural and man-made processes can produce them, but the industrial discharge in this instance is particularly noteworthy. Furthermore, it is often known that the chain of heavy metal pollution travels in a circle, starting with industry and ending with the atmosphere, land, water, food, and humans. Although toxicity is a function of concentration, heavy metals can nevertheless be dangerous at relatively low levels. Particularly in developed countries, the significance of human exposure, intake, and absorption was underlined [6].

III.1.2.2. Environmental pollution:

Heavy metals are harmful to biological systems because they form connections with sulfhydryl groups and produce reactive oxygen species (ROS). This leads to the inactivation of significant macromolecules in addition to oxidative stress and glutathione depletion. When dangerous metals enter the body and are exposed to them, a variety of things happen, such as interactions with or inhibitions of specific metabolic pathways. As a result, numerous detrimental effects on humans and animals are observed. These include cancer, metabolic abnormalities, immune system issues, hormone alterations, specific organ dysfunctions, and congenital illnesses. Therefore, several international bodies regulate the presence of metals in the environment, food supply, and drinking water. Risk assessment studies look at the presence of heavy metals in food and water. It was found that about 21% of them had detectable quantities [6].

III.1.2.3. Environmental impacts of heavy metals:

There are several negative effects when heavy metals are present in the environment. The hydrosphere, lithosphere, biosphere, and atmosphere are all impacted by these effects. In addition to disrupting food networks, health and mortality issues arise until the effects are addressed. The effects of heavy metals on health are summarized in **Figure (III.3)** [2], [9].

III.1.2.4. Effect of heavy metals contamination:

Because of the increased usage and processing of heavy metals in diverse activities to suit the demands of the rapidly expanding population, heavy metal contamination is becoming a major concern on a global scale. The three main environmental compartments that are impacted by heavy metal pollution are the soil, water, and air [2].

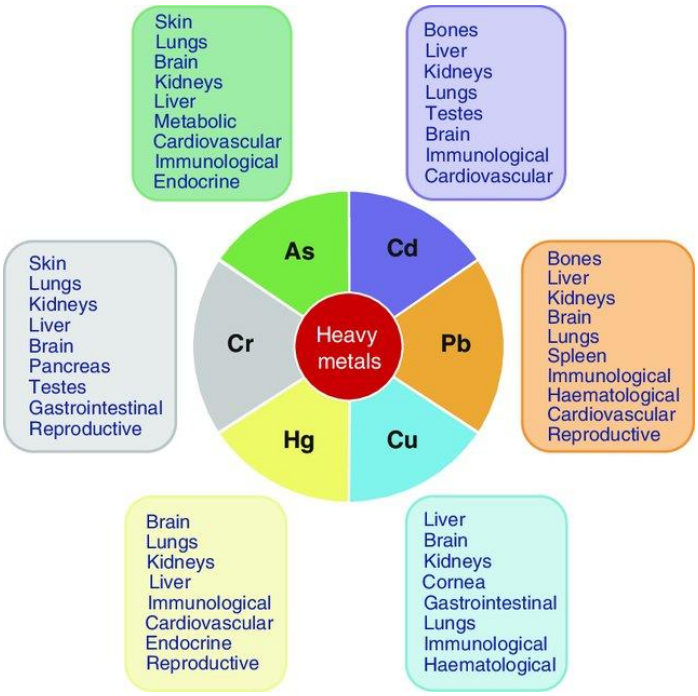

Figure (III.3): *Impacts of heavy metals on the environment* [10].

III.1.2.4.1. Effect on soil:

Heavy metal contamination of soil is caused by emissions from various sources and activities, including mine tailings, industrial operations, the disposal of high metal wastes, leaded gasoline and paints, fertilizer application on land, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, and petrochemical spills. It has been observed that the main sinks for heavy metals discharged into the environment by the aforementioned human activities are soils. Since most heavy metals are not degradable by microbes or chemicals, their overall concentrations remain high for a long period after they are discharged into the environment. Because heavy metals reside in food chains and can devastate an ecosystem, their presence in soils is a major problem. Even while organic pollutants can decompose, the presence of heavy metals in the environment slows down their rate of biodegradation, which doubles the amount of pollution caused by both organic pollutants and the heavy metals. Heavy metals pose a threat to people, animals, plants, and ecosystems in general in a number of ways. These methods include direct ingestion, absorption by plants and food chains, drinking tainted water, and changing the pH, porosity, color, and natural chemistry of soil, all of which have an effect on the quality of the soil [2].

III.1.2.4.2. Effects on water:

Urbanization and industrialization are two of the factors contributing to the elevated level of heavy metal water contamination, despite the fact that there are numerous other sources of contamination. Runoff from cities, towns, and industries carries heavy metals. The majority of these metals wind up building up in water body sediments and soil. Even if they are present in tiny amounts in water sources, heavy metals can nevertheless be extremely harmful to both humans and other organisms. This is due to the fact that a metal's level of toxicity is contingent upon a number of circumstances, including the species to which it is exposed, the metal's nature, its biological function, and the duration of exposure. The interactions between creatures are symbolized by food webs and chains. As a result, all living things are impacted when heavy metals contaminate water. Because heavy metal concentrations rise in the food chain, humans—an example of an organism that feeds at the greatest level—are more vulnerable to major health issues [2].

III.1.2.4.3. Effects on air:

Due to urbanization and industrialization brought on by the world's population development, air pollution has recently become a major environmental issue worldwide. According to reports, dust and particulate matter (PMs), especially tiny particles like PM2.5 and PM10, which are created through both natural and man-made processes, have exacerbated air pollution. Dust storms, soil erosion, volcanic eruptions, and rock weathering are examples of natural processes that release particulates into the atmosphere; manmade activities, on the other hand, are primarily associated to industry and traffic. Because they can cause major health issues such skin and eye irritation, respiratory infections, early death, and cardiovascular disorders, particulate matter is significant and needs specific attention. In addition, these pollutants lead to smog, eutrophication, corrosion, acid rain, and infrastructure degradation. Heavy metals from industrial regions, transportation, and natural sources are among the sources of group 1 metals (Cu, Cd, Pb), group 2 metals (Cr, Mn, Ni, V, and Zn), and group 3 metals (Na, K, Ca, Ti, Al, Mg, and Fe) [2].

Just as heavy metals have an impact on the environment, which we mentioned above, they also pose risks to human health. We can summarize some of the hazardous heavy metals and their sources in **Table (III.2)** [11].

Table (III.2): *Source and impact of most hazardous heavy metals on human health*

Sr. No	Heavy Metal	Source	Impact
1	Mercury (Hg)	Enters the environment through the leaching of soil due to acid rain, coal burning, or industrial, household, and mining wastes	Causes damage to nervous system, kidneys, and vision
2	Lead (Pb)	Sources include paint, mining wastes, and incinerator ash, water from lead pipes and solder, and automobile exhaust.	Causes damage to kidneys, nervous System, learning ability, ability to synthesize protein, and nerve and red blood cells.
3	Cadmium (Cd) .	Sources include electroplating, mining, and plastic industries, as well as sewage	Causes kidney disease
4	Arsenic (As)	Enters the environment through herbicides, wood preservatives, and mining industry	Causes damage to skin, eyes, and liver. May also cause cancer. .
5	Antimony (Sb)	Enters the environment through mining and ore processing industry	Can irritate eyes, skin, and lungs can also cause heart problems, stomach pain, diarrhea, vomiting, and stomach ulcers
6	Chromium (Cr)	Source includes cement industry, Effluents from chemical plants, tobacco smoke and contaminated land fill.	Can Cause Pulmonary fibrosis, lung cancer.

III.2. Adsorption and Catalysis in Heavy Metal Removal Using PVP-coated ZnO Nanocomposites:

III.2.1. Adsorption Mechanism for Heavy Metal Removal:

Ion exchange, chemical precipitation, flotation, electrochemical deposition, adsorption, and other techniques are among the several industrially employed techniques for heavy metal removal. All of these industrial processes are costly and can result in a significant amount of sludge that requires additional treatment. One of the future methods for treating wastewater that contains heavy metals is the adsorption technique [11].

III.2.1.1.Adsorption:

Adsorption is the process by which atoms, ions, or molecules of dissolved solids from liquids adhere to the surface of solids; in other words, it is a mass transfer process wherein the dissolved solid from liquid is deposited on the surface of solids due to physical or chemical interaction.

When choosing an adsorbent to treat wastewater, the two main considerations in this procedure are cost-effectiveness and technical suitability. Adsorbents come in various forms and are categorized as biological, industrial, agricultural, and natural materials [11].

III.2.1.1.1. Adsorption on Natural materials:

Numerous studies have demonstrated that limestone is a natural geological element that works well for treating heavy metal-contaminated water. However, for extensive remediation activities, the reported metal-removal effectiveness of limestone is lower than desired or anticipated, especially when considering the basic parameters influencing sorption processes.

Many researchers have studied the effects of mechanically grinding natural Serbian clay on the removal of heavy metals from an aqueous medium. According to this study, Cd and Ni were only absorbed at 81% of their initial concentration, but Cr and Pb were completely absorbed at approximately 98% of their initial concentration. It was discovered that the wastewater from the palm oil mill may contain more than 50% of Zn (II) and Mn(II) and more than 60% of Fe(III) that can be removed using natural zeolite. Many researchers are working on removing heavy metals from natural materials [11].

III.2.1.1.2. Adsorption on Industrial waste:

Many researchers are interested in using inexpensive adsorbent materials made from industrial waste to remove heavy metal ions from wastewater instead of traditional costly

methods. The following materials have shown promise: fly ash, waste clay, red mud, lignin, beet pulp, blast furnace slag, tea industry waste, and sugarcane bagasse. One of the researchers studied the ability of Turkish coal ash to extract nickel [Ni (II)], copper [Cu (II)], and zinc [Zn (II)] from an aqueous solution. The results showed that the fly ash with the highest calcium content was as effective in adsorbing metals as activated carbon.

The effect of four factors (the mass ratio between fly ash and lime, the type of adsorbent containing fly ash and lime, the solution temperature, and the adsorbent concentration) on the removal of five metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) was studied. It was found that for an adsorbent ratio of 0.66, an adsorbent content of fly ash and 5% lime by mass, approximately 122 grams per liter, and a solution temperature of 66 degrees Celsius, high adsorption and low loss resulted. Afterwards, the feasibility of removing organic chemicals, heavy metals, dyes, and harmful anions from water using activated carbon made from Jatropha husks, which is an industrial agricultural solid waste, was investigated.

According to the study, 61% of the initial concentration of chromium IV and 97% of nickel can be removed.

The removal of heavy metals from wastewater using industrial waste has been the subject of numerous investigations [11].

III.2.1.1.3. Adsorption on biological and agricultural waste:

The use of agricultural by-products as adsorbents has recently garnered significant attention in studies aimed at removing heavy metals from industrial wastewater.

Biosorption is a process for treating heavy metals using agricultural by-products. Some biomass can concentrate and bind pollutants passively to its cellular structure through a physicochemical process called biosorption. Many studies believe that this phenomenon will aid in environmental remediation and provide a cost-effective alternative for removing harmful heavy metals from industrial wastewater. The adsorption capacities of pectin-rich fruit peels were examined and compared, and it was found that grape peels have the highest capacity to absorb heavy metals like cadmium compared to other fruit peels such as orange, lemon, apple, etc. A study was also conducted comparing the capacity to remove heavy metals from sawdust and rice husk, and it was found that due to the functional silica group on rice husk and its large surface area, most heavy metals, including Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}, have a higher absorption capacity for rice husk compared to sawdust. The bioremediation and biosorption process of chromium (VI) was investigated using new biosorbent materials from raw rutin and rutin resin. It was reported that the crude rutin and rutin resin had corresponding biosorption

capacities of 26.3 and 41.6 mg/g, respectively. The primary functional groups associated with the resin for chromium extraction from wastewater were hydroxyl, carboxyl, and carbonyl groups. It was also suggested to use chemically modified agricultural waste (okra residue) to remove harmful heavy metal ions from the aqueous solution. They found that the biomass had a very high absorption capacity for lead Pb^{2+} (273.97 mg/g), followed by cadmium Cd^{2+} (121.51 mg/g), copper Cu^{2+}, and zinc Zn^{2+} (72.72 and 57.11 mg/g, respectively).

When comparing low-cost biosorbent materials such as algae (Ascophyllum nodosum), wood chips, and reed roots (Phragmites australis), it was found that wood chips had a very good absorption capacity for lead, while algae had the highest absorption capacity for cadmium. Because different groups assist in the bioremediation of various metals, such as silica, which has a greater affinity for sulfur, zinc, and copper; hydroxyl, which has a greater affinity for chromium; and nitro, which has a greater affinity for lead, the removal of heavy metals through bioremediation depends on the functional group associated with the biosorbent materials.[11]

III.3. Removal of Heavy Metals from Petroleum Wastewater

III.3.1. Preparation of Suspensions of ZnO NPs and ZnO@PVP NCs

To ensure high quality, ultrapure water is used for the initial preparation of nanoparticle suspensions. During preparation, nanocomposites typically form clusters at the bottom of the container. These clusters must be broken down and dispersed to make the nanocomposites suitable for various applications. Effective dispersion is achieved through sonication, a technique that utilizes ultrasonic waves. Specifically, for ZnO nanoparticles (NPs) and ZnO@PVP nanocomposites (NCs), which tend to form aggregates or agglomerates, it is critical to break down these structures at the particle level to achieve optimal dispersion for the removal of heavy metals from petroleum wastewater. For experimental purposes, 5 mg of nanocomposites is prepared in 1 mL of distilled water.

III.3.2. Equipment used: ICP-MS (NexION 2000, HTDS)

The Inductively Coupled Plasma Mass Spectrometer (ICP-MS), model NexION 2000, provided by HTDS (**Figure (III.4)**), is a highly sensitive analytical instrument used to determine the concentration of metallic elements, such as heavy metals, in samples. It combines inductively coupled plasma (ICP) technology with mass spectrometry (MS) to deliver precise measurements down to parts per trillion (ppt).

Figure (III.4): *Image of the NexION 2000 ICP-MS Spectrometer.*

III.3.2.1. Operating Mechanism:

1. Sample Preparation: The sample (e.g., petroleum wastewater) is injected through a 0.5 mL injector into a cooled spray chamber.
2. Nebulization and Vaporization: The sample is transformed into a fine mist using a nebulizer and a variable-speed peristaltic pump, then introduced into the plasma generated by high-purity argon gas (99.9999% purity).
3. Ionization: In the plasma (temperature reaching 6,000–7,000 K), the sample vaporizes, and atoms are ionized to form ions.
4. Ion Separation and Analysis: Ions are transferred to the mass spectrometer, where they are separated based on their mass-to-charge ratio (m/z) and detected with high precision.
5. Gas Management: The instrument includes a flow regulator for gases (nebulizer gas, plasma gas, and auxiliary gases) to ensure plasma stability.
6. Impurity Removal: An extractor removes impurities, and Kinetic Energy Discrimination (KED) mode is used to minimize interferences.

III.3.2.2. Main Components:

- Water-cooled spray chamber for sample cooling.
- Nebulizer with a peristaltic pump for sample nebulization.
- Valve system and 0.5 mL injection loop.

- High-purity gas cylinders (argon and helium).
- Syngistix software for data analysis.
- 20 mL polypropylene tubes for sample storage.

III.3.2.3. Applications:

The ICP-MS is used to analyze industrial wastewater, such as petroleum wastewater, to determine the concentration of heavy metals (e.g., As, Cd, Pb) with high accuracy. This facilitates the evaluation of the efficiency of adsorbents like ZnO NPs in heavy metal removal. The instrument's ability to analyze multiple elements simultaneously makes it ideal for environmental research.

III.3.3. Adsorption Mechanism of Heavy Metals on ZnO@PVP NCs:

The adsorption process of heavy metals from petroleum wastewater using ZnO@PVP nanocomposites (NCs) involves a series of sequential steps influenced by surface chemistry and mass transfer phenomena, as illustrated in (**Figure (III.5)**). Initially, ZnO@PVP NCs are introduced into the wastewater, where they interact with heavy metal ions over a 30-minute contact period, followed by centrifugation to separate the loaded nanocomposites, as depicted in the experimental setup of (**Figure (III.5)**) [12]. The mechanism governing this interaction is detailed through four distinct stages [9], [13]:

A. **External Diffusion**: Heavy metal ions in the bulk wastewater migrate toward the ZnO@PVP NCs, driven by concentration gradients and aided by convective mixing, as the solution is stirred.

B. **Internal Diffusion**: The ions penetrate the liquid boundary layer surrounding the nanocomposite, reaching the external surface through diffusion across this interfacial film.

C. **Surface Diffusion**: Once at the surface, the ions diffuse across the outer layer of the ZnO@PVP NCs, navigating the PVP coating and accessing the ZnO core, where migration occurs along the surface to available sites, influenced by surface charge interactions.

D. **Adsorption (Fixation):** The heavy metal ions bind to specific adsorption sites on the ZnO core, facilitated by electrostatic attractions and ion exchange, resulting in their effective immobilization.

This multi-step process, culminating in the formation of a ZnO@PVP NCs-heavy metal complex, underscores the efficacy of the nanocomposites in wastewater

treatment, leveraging both the adsorptive properties of ZnO and the stabilizing role of PVP [14], [15].

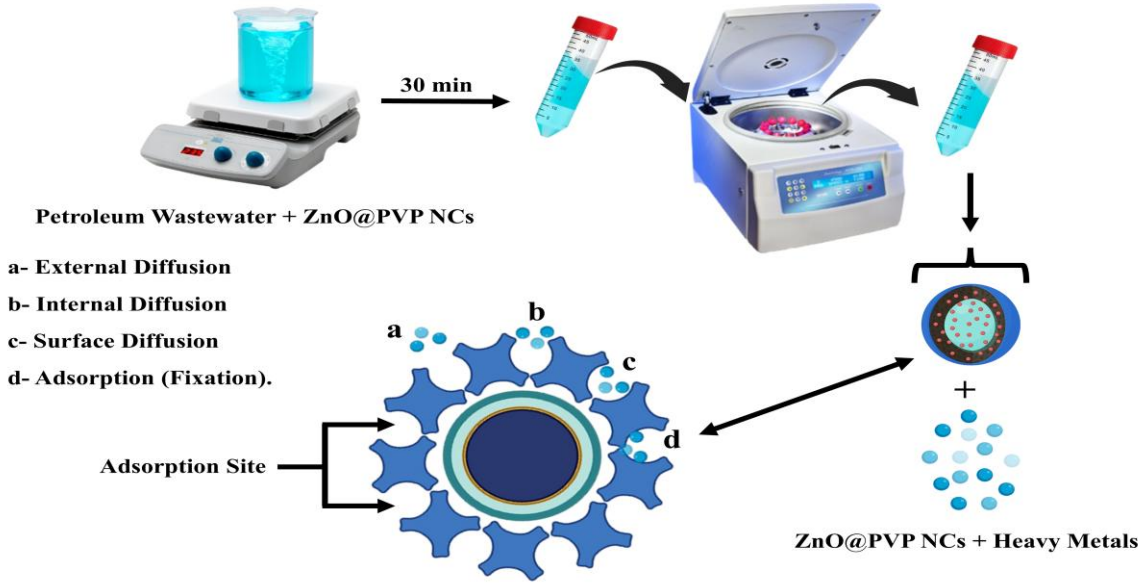

Figure (III.5): *Schematic of the adsorption mechanism of heavy metals on ZnO@PVP NCs nanocomposites: surface charge effects and diffusion steps* [16].

III.4. Results and Discussion

The kinetics of heavy metal extraction, including As(III), Be(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II), and Zn(II), were examined using 5 mg of ZnO nanoparticles (NPs) and ZnO@PVP nanocomposites (NCs) in contact with ion solutions over varying durations. (***Figure (III.6)***) depicts the time-dependent removal of these metals from solution, with (a) ZnO NPs and (b) ZnO@PVP NCs. The data reveal that approximately 80% of the adsorption occurs within 5 to 10 minutes for both materials. Metals such as Be, Cr, Mo, Sb, and Se exhibit rapid uptake, approaching saturation early, while As, Cd, Mn, Ni, Pb, and Zn show a more gradual increase over time. The ZnO@PVP NCs demonstrate a slightly faster initial adsorption rate for Cd, Mn, and Ni, likely due to enhanced surface interactions facilitated by the PVP coating, highlighting the temporal advantage of the nanocomposite in practical applications [12].

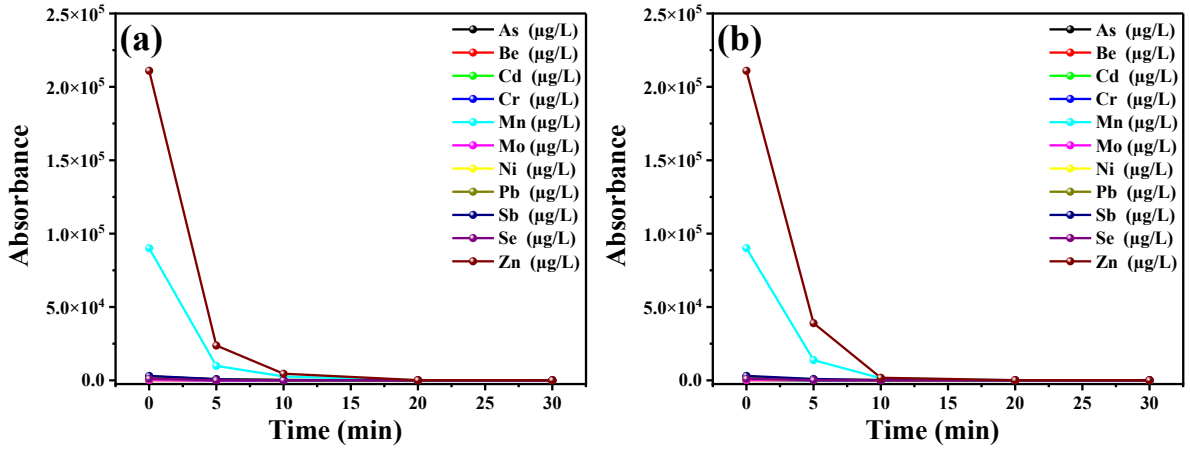

Figure (III.6): *Schematic of the adsorption mechanism of heavy metals on ZnO@PVP NCs nanocomposites: surface charge effects and diffusion steps*

The adsorption performance of ZnO nanoparticles (NPs) and ZnO@PVP nanocomposites (NCs) was evaluated for the removal of As(III), Be(II), Cd(II), Cr(VI), Mn(II), Mo(II), Ni(II), Pb(II), Sb(III), Se(-II), and Zn(II) from ion solutions using 5 mg of each material. (**Figure (III.7)**) illustrates the heavy metal removal efficiency over time, with (a) ZnO NPs and (b) ZnO@PVP NCs, with detailed efficiencies presented in Table 1. Both materials achieve efficiencies exceeding 99.9% within 30 minutes under optimal conditions. ZnO NPs yield efficiencies of 99.95% for As, 100% for Be, Cr, Mo, Sb, and Se, and 99.91–99.96% for Cd, Mn, Ni, Pb, and Zn. In comparison, ZnO@PVP NCs slightly outperform with 99.94% for Cd and Ni, and 99.93% for Mn, reflecting the subtle enhancement imparted by the PVP layer. These results confirm the exceptional capacity of both nanomaterials as adsorbents for environmental remediation [12], [14].

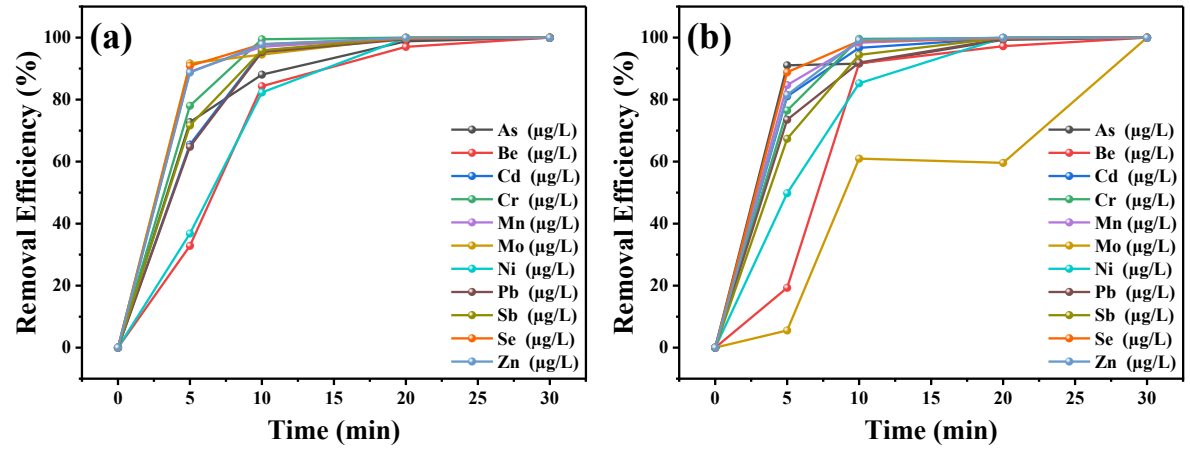

Figure (III.7): *Heavy metal removal efficiency over time using: (a) ZnO NPs and (b) ZnO@PVP NCs*

Table (III.3): *Removal Efficiency of Heavy Metals by ZnO Nanoparticles (NPs) and ZnO@PVP Nanocomposites (NC*

	Removal Efficiency (%)	
Heavy Metals	ZnO NPs	ZnO@PVP NCs
As	99.95	99.95
Be	100.00	100.00
Cd	99.93	99.94
Cr	100.00	100.00
Mn	99.91	99.93
Mo	100.00	100.00
Ni	99.93	99.94
Pb	99.92	99.92
Sb	100.00	100.00
Se	100.00	100.00
Zn	99.96	99.96

III.5. Conclusion :

This study confirmed the superior performance of polyvinylpyrrolidone-coated zinc oxide nanoparticles (ZnO@PVP NCs) in effectively removing heavy metal ions from petroleum wastewater. Experimental analyses conducted using UV-Vis spectroscopy demonstrated enhanced light absorption in the UV-Vis region for ZnO@PVP NCs compared to uncoated ZnO nanoparticles. This improvement enhances their suitability for adsorption and photocatalytic applications, positioning ZnO@PVP NCs as promising materials for environmental remediation and optical applications. The ZnO@PVP nanocomposites exhibited exceptional adsorption and photocatalytic capabilities, achieving a removal efficiency exceeding 99.9 By integrating adsorption and photocatalysis, these composite nanomaterials offer a robust and efficient approach to addressing complex water pollution challenges. The enhanced properties of ZnO@PVP NCs pave the way for advanced wastewater treatment strategies, contributing to improved water quality and a cleaner environment.

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GENERAL CONCLUSION

General Conclusion and Future Perspectives

In response to the pressing global challenge of environmental pollution, nanotechnology has emerged as a pivotal field, integrating advanced methodologies from chemistry, physics, and materials science to develop innovative solutions. The synthesis and application of nanomaterials, particularly those within the size range of 1–100 nm, have opened new avenues for addressing complex environmental issues, such as water contamination by heavy metals and organic pollutants. This study has successfully demonstrated the potential of polyvinylpyrrolidone (PVP)-coated zinc oxide (ZnO) nanoparticles (ZnO@PVP NCs), synthesized via the co-precipitation method, as highly effective materials for environmental remediation.

The comprehensive characterization of ZnO@PVP NCs, employing techniques such as UV-Vis spectroscopy, FTIR spectroscopy, and X-ray diffraction (XRD), has validated their enhanced physicochemical properties. The incorporation of PVP as a coating material significantly improved the optical properties of ZnO nanoparticles, as evidenced by a characteristic absorption peak at 361 nm and a reduced bandgap from 1.94 eV to 1.81 eV. These optical enhancements, coupled with strong chemical interactions between the ZnO core and PVP coating, confirmed by shifts in vibrational bands of O–H and C=O functional groups, contribute to the stability and functionality of the nanocomposites. Moreover, XRD analysis affirmed that the hexagonal wurtzite structure of ZnO remained intact, underscoring the compatibility of the PVP coating with the crystalline integrity of the nanoparticles. These findings highlight the efficacy of PVP coating in tailoring the properties of ZnO nanoparticles, making them promising candidates for photocatalytic and adsorption-based applications.

The application of ZnO@PVP NCs in the removal of heavy metal ions from petroleum wastewater further demonstrated their superior performance, achieving removal efficiencies exceeding 99.9% under optimal conditions. By integrating adsorption and photocatalysis, these nanocomposites offer a robust and efficient approach to mitigating water pollution, particularly for toxic heavy metals such as As(III), Cd(II), Cr(VI), and Pb(II). The enhanced light absorption in the UV-Vis region and improved charge carrier dynamics position ZnO@PVP NCs as versatile materials for advanced wastewater treatment strategies, contributing to improved water quality and environmental sustainability.

Looking ahead, future research should focus on optimizing the synthesis parameters of ZnO@PVP NCs to further enhance their photocatalytic and adsorption efficiencies. Key

parameters, such as PVP concentration, pH, reaction time, and calcination conditions, warrant systematic investigation to fine-tune the morphology, dispersion, and surface properties of the nanocomposites. Additionally, exploring the scalability of the synthesis process and evaluating the performance of ZnO@PVP NCs in real-world environmental applications, such as industrial wastewater treatment plants, will be critical for practical implementation. The integration of ZnO@PVP NCs with other nanomaterials or hybrid systems could also be explored to develop multifunctional platforms for simultaneous pollutant removal and water purification. Furthermore, assessing the long-term stability, recyclability, and environmental impact of these nanocomposites will ensure their viability as sustainable solutions for environmental remediation.

In conclusion, this study underscores the transformative potential of ZnO@PVP NCs in addressing environmental challenges through nanotechnology. By bridging the disciplines of chemistry, materials science, and environmental engineering, these nanocomposites pave the way for innovative, efficient, and sustainable strategies to combat water 1 pollution, thereby contributing to the preservation of ecosystems and the promotion of a cleaner environment.