



People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
Echahid Hamma Lakhdar University - El Oued
Faculty of Technology
Department of Process Engineering and Petrochemistry



Final Study Thesis

In view of obtaining the degree of

ACADEMIC MASTER

Field: Science and Technology

Specialization: Process Engineering

Major: Chemical Engineering

Presented by:

Guessoum Souheyla

Laghribi Chahrazad

Subject:

Evaluation of the effectiveness of plasma-nanoparticle coupling for the treatment of industrial wastewater

Before the Jury :

Dr. Chaabia Nacer	Chairperson	University of El Oued
Pr. Laouini Salaheddine	Examiner	University of El Oued
Pr. FERHAT Med Fouad	Supervisor	University of El Oued

2024/2023

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ
الْحَمْدُ لِلَّهِ الَّذِي
خَلَقَ الْمَوَدَّعَةَ
الْحَمْدُ لِلَّهِ الَّذِي
خَلَقَ الْمَوَدَّعَةَ



Appreciation and thank

The Most Gracious, the Most Merciful

Praise be to Allah, abundant and good praise, and thanks to Him who granted us the strength, knowledge, and determination to complete our modest work. We extend our heartfelt thanks to everyone who contributed, even a little, whether directly or indirectly, to this work

*First, we express our sincere thanks to our esteemed professor, **Dr. Farhat Mohamed Fouad**, our supervisor, for his advice, guidance, and direction throughout our university journey and during the preparation of this thesis. Thanks also go to Professor **BenKhira LAtra** and Professor **Hamoudi Ammar Said**, who helped us and provided us with a lot of information and advice*


*We extend our sincere thanks and appreciation to the Director of our university, **ALCHAHD Hamma Lakhdar University, Dr. Omar Farhati**; the Dean of our faculty, the Faculty of Science and Technology, **Dr. Ali Chamsa**; the Head of our department, the Department of Process and Petrochemical Engineering, **Dr. Salah Eddine Laouini** and to **Dr. Ben Mya .Ammar***

We express our thanks to all our professors, those who taught us and those who did not, each by name, for their efforts throughout the five-year journey. Thanks also go to the administrative staff, laboratory workers, and the university business incubator staff for their utmost thanks and appreciation

We thank our esteemed family for their moral, material, and psychological support. We are here thanks to the prayers of our parents

Thanks to all the companions and friends, each by name, for the good company

throughout these years





Dedication

Alhamdulillah for the achievement, and Alhamdulillah at the beginning and at the end

*To my pure angel and my strength in life after Allah, my first and eternal supporter, I dedicate this achievement to you. Without your sacrifices, it wouldn't have existed. To my dear mother, **Faouzia***

*To the one who bears my name, to the one who illuminated my paths and my life, to my dear father, **Faouzi***

*.To my second father, my support, and my dear brother, **Khaled***

*To my second brother, **Mohamad El Hadi**, and my sweet little sister **Amani**, and my younger siblings, **Ahmed Yassin**, **Youssef** and **Basmalat Arhman***

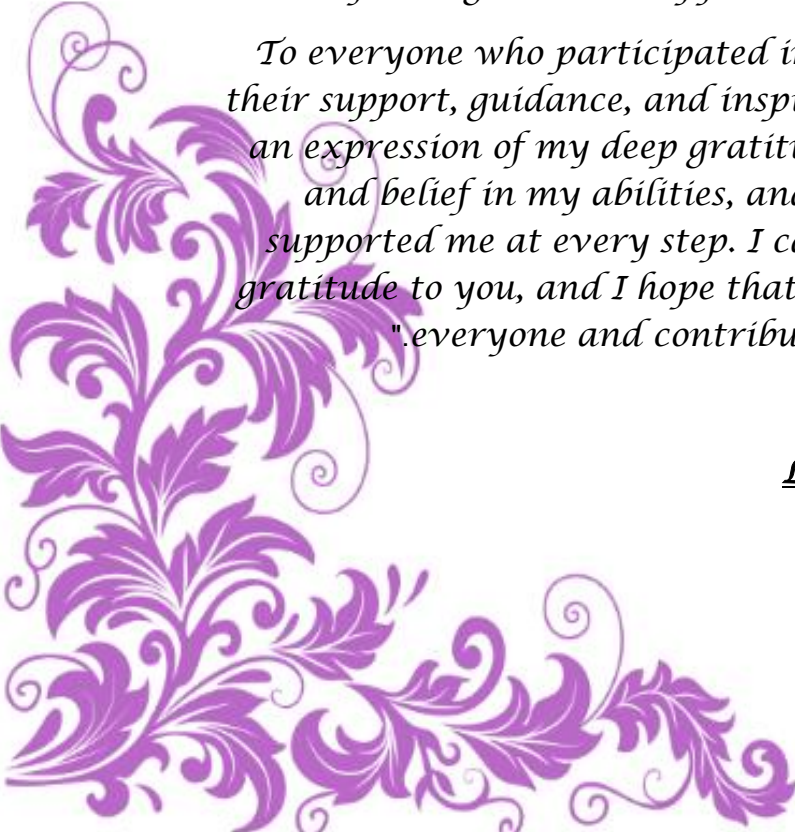
*To my friend and partner in the thesis accomplishment, **Souheyla***

*To my beloved, the love of my soul, and my friend, **WISSal**, and to all my other friends, **Asma**, **Ibtihal**, **HadIL**, **Hanadi**, **Doaa**, **Hanine** and **Izdihar***

*.To my dear guide and supporter, the inspector, **Nadia Ramli***

To everyone who participated in my academic journey, with their support, guidance, and inspiration, I dedicate this thesis as an expression of my deep gratitude. Thank you for your trust and belief in my abilities, and for your wise words that supported me at every step. I can only express my immense gratitude to you, and I hope that this work will be beneficial to everyone and contribute to our shared field

Laghríbi Chahrazad





Dedication:

Praise be to Allah, abundant praise. The journey was not short, nor should it have been. The dream was not close, nor was the path paved with ease, but I did it

*To the one who stayed up nights to light my way, to the one whose prayers fortified me, to the one who shared my joys and sorrows, to the source of compassion and tenderness, the most wonderful woman in existence, my dear mother, **Wahiba***

*To the one who taught me that life is struggle and that its goodness lies in knowledge and education, to the one who never withheld anything from me, to the greatest and most cherished man in the world, my dear father, **Mohammed Al-Amin***

*To the hidden hand that removed thorns from my path, my kind grandmother, **Rokia**. To the one who carries the scent of my father, my dear aunt, **Fatima Al-Zahra***

*To my steadfast rib, my support in life, my loyal brother, **Boussairi**. To my second support and my unwavering right shoulder, my brother, **Abdel Mounaam***

*And to the flowers of my life, my joy and smiles, my three sisters, **Yousra, Massaouda, and Kamilia**, and to all my other dear siblings*

*To my partner in accomplishing this work, my friend, **Chahrazad***

*To the sister my mother did not give birth to, to my gentle **Hadil**. To all my friends and my butterfly, my sweet friend, cousins, and to my everlasting joy*

I want to express my deep gratitude and appreciation to you all. You are my heart and soul, and I thank you for all your invaluable support and love. You are the essence of my life, and I am forever grateful to you

Quessoum Souheyla



List of figures	Page number
Fig-1. Size comparison of different structures (living and nonliving).	6
Fig- 2. Overview of commonly used nanoparticle (NP) type, classified as organic, or composite structures.	7
Fig-3. Characteristics of Nanoparticles	8
Fig- 4. Energy generation approaches from (A) Piezoelectrics actuators (B) Water splitting (C) CO ₂ reduction.	8
Fig-5. The difference between plasma and gas.	10
Fig-6. System for DC glow discharge	11
Fig-7. Capacitive coupled discharge system	12
Fig-8. Inductively coupled discharge system	12
Fig-9. Three basic configurations	13
Fig-10. Conventional and advanced techniques used for wastewater treatment	24
Fig-11. General mechanism of adsorption to remove contaminants	25
Fig-12. General mechanism of adsorption to remove contaminants	25
Fig- 13. General mechanism of coagulation/flocculation to remove contaminants	26
Fig- 14. Textile wastewater treatment by advanced oxidation process	26
Fig- 15. Biofilm for sewage water treatment	27
Fig-16. Schematic of the gliding arc discharge reactor	33
Fig-17. The synthesized nanoparticle powder	34

List of Curves	Page number
Cur-1. (a) Plot of $(\alpha h\nu)^2$ versus photon energy of synthesized ZnO. (b) Inset shows the Urbach energy plot of $\ln(\alpha)$ versus $(h\nu)$	38
Cur-2. FTIR spectra of ZnO NPs and inset shows the enlarged spectra in the range $<600 \text{ cm}^{-1}$.	39
Cur-3. X-ray diffraction pattern of ZnO NPs	40
Cur-4. SEM image of the ZnO NPs plasma synthesized with a magnification of (a) 100.00 KX; (b) their corresponding particle size distribution and (c) Atomic concentration and Typical EDAX spectra.	41
Cur-5. (a) Absorbance spectra of dye solution under daylight irradiation, (b) photocatalytic degradation of dye at different times	42
Cur-6. (a) Absorbance spectra of dye solution under plasma, (b) photocatalytic degradation of dye at different times.	43
Cur-7. (a) Absorbance spectra of dye solution under plasma with catalyste (b) photocatalytic degradation of dye at different times	45

List of Symbols	
NPs	nanoparticles
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
IR	Infrared
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
BET	Brunauer Emmett Teller
POM	Polarized Optical Microscopy
EDX	Energy dispersive X-ray
AFM	Atomic Force Microscopy
DLS	Dynamic Light Scattering
PL	Photoluminescence
UV-Vis	Ultraviolet-Visible Spectroscopy
FTIR	Fourier Transform Infrared
DBD	dielectric barrier discharge
ZnO	Zinc Oxide
DC	direct current
CCD	Capacitive Coupled Discharge
ICD	Inductively Coupled Discharge
NO _x	Nitrogen Oxides
DNA	Deoxyribonucleic Acid
SF ₆	Sulfur Hexafluoride
CF ₄	Carbon Tetrafluoride
LEDs	light-emitting diodes
GAD	Generalized Anxiety Disorder
MB	Methylene Blue

List of Tables	Page nombre
Table-1. Pollutants and its Sources	24

Table of Contents	Page numbre
Table of figures	III
List of Curves	I
List of Symbols	II III
List of Tables	II
List of Contents	III
Introduction	1
<i>Theoretical part</i>	
<i>Chapter I: Integration of Plasma and Nanoparticles</i>	
Introduction	5
I.1 Nanomaterials	5
I.1.1 Definition of nanomaterials	5
I.1.2 Nanoparticle Classifications	6
I.1.2.1 Carbon-Based	
I.1.2.2 Metallic	6
I.1.2.3 Metal Oxide Synthesis	6
I.1.2.4 Ceramics	6
I.1.2.5 Semiconductor	6
I.1.3 Characteristics of Nanoparticles	7
I.1.4 Applications of Nanoparticles	8
I.2 Plasma	9
I.2.1 Definition	9
I.2.2 Structure and composition of plasma	10
I.2.3 Properties of plasma	10
I.2.4 Plasma Generation Techniques	11
I.2.5 Applications of plasma	13
References I	16
<i>Chapter II: Synthesis of ZnO nanoparticles by cold plasma and their application</i>	
Introduction	19
II.1 Zinc oxide (ZnO) nanoparticles	19
II.1.1 Synthesis of ZnO nanoparticles by cold plasma	19
II.1.2 Principles of cold plasma synthesis	20
II.1.3 Parameters influencing the synthesis of nanoparticles	20
II.1.4 Characterization of ZnO nanoparticles	21
II.2 Wastewater Treatment	22
II.2.1 Difinition	22
II.2.2 Wast water pollutants	23

II.2.3 Different methods for treating industrial wastewater	24
II.2.3.1 Physical methods	24
II.2.3.2 Adsorption	25
II.2.3.3 Membrane Filtration	25
II.2.3.4 Chemical method	26
II.2.3.5 Electrochemical oxidation	26
II.2.3.6 Photo-electrochemical oxidation	26
II.2.3.7 Fenton's oxidation	27
II.2.3.8 Biological method	27
References II	28
<i>Practice Part</i>	
<i>Chapter I: Materials and methods</i>	
Introduction	32
I.1. Material	32
I.2. Methods	33
I.2.1. Synthesis of ZnO nanoparticles by cold plasma	33
I.2.2. Characterizations	34
I.2.3. Photocatalytic activity	35
I.2.3.1 Under daylight	35
I.2.3.2 Under plasma	35
References III	36
<i>Chapter II: Results and discussion</i>	
II.1 Characteristics of the synthesized ZnO	38
II.1.1 UV-visible study	38
II.1.2 FTIR Spectroscopic Analysis	38
II.1.3 X-ray diffraction	39
II.1.4 Scanning Electron Microscopy (SEM) + EDAX	40
II.2 Photocatalytic activity	41
II.2.1 Under daylight	41
II.2.2 Under plasma	42
Conclusion	46
Abstract	.

Introduction:

Industrial wastewater varies significantly in terms of flow and pollution levels, making it difficult to determine fixed values for its components. Typically, this water may contain suspended, colloidal, and dissolved solids, both inorganic and organic. The water may be highly acidic or alkaline and contain varying amounts of colored substances. It may also include inert, organic, toxic materials, or pathogenic bacteria. This wastewater can be discharged into the sewage system, provided it does not adversely affect treatment efficiency or cause system issues. In some cases, pre-treatment of the waste may be necessary before discharge into the municipal system, or complete treatment may be required when discharging directly into surface or groundwater. [1]

There is an urgent need to develop new and innovative water treatment technologies to ensure a continuous supply of pure drinking water. Additionally, the damage and limitations associated with chemical water treatment processes are well known. Recent trends in nanotechnology indicate the effectiveness of nanomaterials, such as nano-adsorbents, nano-metals, nano-membranes, and photocatalysts, in various processes. This chapter considers these factors and aims to summarize the use of nanoparticles in industrial wastewater treatment. [2]

Interest in nanotechnology has increased significantly due to its unique properties, enabling its use in various fields, including the chemical, mechanical, and technological industries. Additionally, it has been employed in the medical field and pharmaceutical industry. Among the common nanomaterials, zinc oxide has gained considerable fame in scientific and medical circles due to its prominent role in biomedical applications and antibacterial properties. This importance is due to its unique chemical and physical properties, such as high electrochemical coupling coefficient, high photostability, and chemical stability. There are several methods for preparing zinc oxide nanoparticles (ZnO,NPs). [3]

A simple precipitation method using non-thermal plasma (NTP) technology, specifically the Gliding Arc Discharge (GAD) method, has been developed, where distilled water is used as a solvent and moist air as a carrier gas in a two-step protocol. This method is promising due to its high production yield, short synthesis time, and low protocol cost. [4]

In this study, various spectroscopic analyses have been employed to assess the effectiveness of the plasma-nanoparticle coupling for wastewater treatment. Spectroscopic techniques such as UV-Vis spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) have been utilized to characterize the chemical composition and structural changes in the treated wastewater samples. These analytical tools provide valuable insights into the

degradation mechanisms of organic pollutants and the overall efficiency of the treatment process.

By evaluating the effectiveness of plasma-nanoparticle coupling for industrial wastewater treatment, this memorandum aims to contribute to the development of innovative and sustainable solutions for environmental remediation challenges. The findings of this study are expected to inform future research directions and guide the implementation of advanced wastewater treatment technologies in industrial settings.

This study addresses, in the theoretical part, first how to integrate plasma technology with nanoparticles, then focuses on the process of manufacturing ZnO nanoparticles using cold plasma. In the practical part, we will review the materials and methods used in the experiments, as well as the obtained results and their detailed discussion.





Chapter I
Integration of Plasma
and Nanoparticles

Introduction

The integration between plasma and nanoparticles represents an important field in scientific research and advanced technological applications. This topic explores how plasma interacts with nanoparticles and how this interaction can be utilized in a variety of applications, such as energy, medicine, electronics, manufacturing, and more. Applications range from modern information technology uses to the development of materials and healthcare products capable of enhancing performance or introducing new properties. A profound understanding of the interactions between plasma and nanoparticles is required to achieve effective and innovative applications in various fields.

1.1 Nanomaterials:

1.1.1 Definition of nanomaterials:

Nanotechnology focuses on the development and utilization of structures and devices on a scale between individual molecules and about 100 nanometers, where new properties emerge. Custom nanostructures and devices can be built by controlling at the atomic and molecular levels. Nanotechnology is recognized as an advanced and efficient technology, arising from the scientific convergence of physics, chemistry, biology, materials, and engineering at the nanoscale.

The manufacturing of nanoparticles is crucial for generating structured nanomaterials, and they have been empirically produced over the years. Nanoparticles find applications in various fields such as advanced materials, electronics, biotechnology, pharmaceuticals, and sensing. Nanotechnological techniques already impact high-tech industries, including hard disks, imaging systems, information recording, advanced drug delivery, chemical-mechanical polishing, inkjet technologies, and chip systems. [5]

Nanoparticles are particles with a diameter equal to or less than 100 nanometers, imparting enhanced properties to composite materials. A diverse range of inorganic particles has been utilized to prepare nanocomposites of the polymer/inorganic particles type, including metal particles such as aluminum, iron, gold, and silver, as well as metal oxide particles like zinc oxide, aluminum oxide, calcium carbonate, and titanium dioxide, in addition to non-metallic particles. The selection of nanoparticle depends on

the desired thermal, mechanical, electrical properties, and application of the nanocomposites. [6]

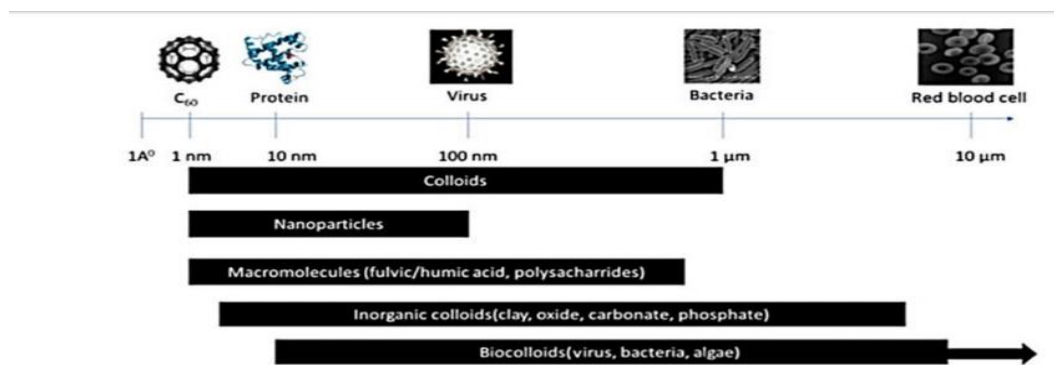


Fig-1. Size comparison of different structures (living and nonliving). [7]

I.1.2 Nanoparticle Classifications:

I.1.2.1 Carbon-Based:

Fullerenes: Spherical carbon molecules.

Graphene: Two-dimensional hexagonal lattice.

Carbon Nanotubes: Hollow coils of graphene.

I.1.2.2 Metallic:

- Synthesized from metals like aluminum and gold.

- Size 10-100 nanometers, crystalline structures, and electrical properties.

I.1.2.3 Metal Oxide Synthesis:

- Metals like copper and silver used for antibacterial purposes.

- Study of metal oxides for electrochemical detection and medical applications.

I.1.2.4 Ceramics:

- Non-metallic solids used in catalysis and photochemical reactions.

I.1.2.5 Semiconductor:

- Properties between metals and non-metals.

- Polymer particles efficient in water splitting and electronics.

- These classifications showcase the versatility of nanoparticles across diverse fields, from medicine to catalysis. [8]

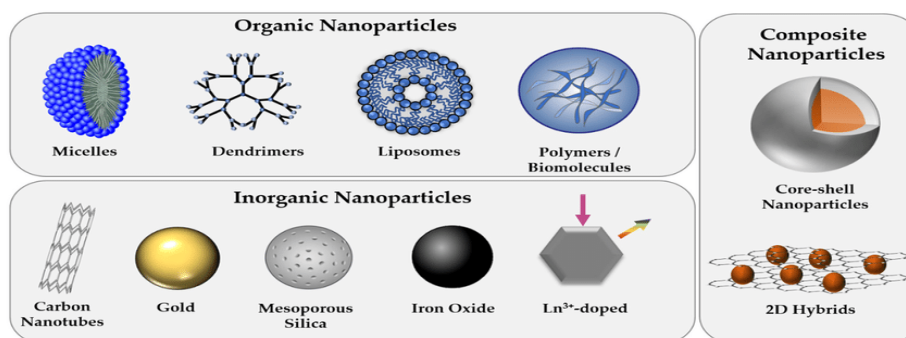


Fig- 2. Overview of commonly used nanoparticle (NP) type, classified as organic, or composite structures. [9]

I.1.3 Characteristics of Nanoparticles:

Multiple techniques are employed to analyze the physicochemical properties of nanoparticles (NPs). These include X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Infrared (IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Brunauer Emmett Teller (BET) for measuring particle size. In morphological studies, Polarized Optical Microscopy (POM), SEM, and TEM are crucial. SEM relies on electron scanning to provide precise information about nano-level particles, while TEM, based on electron transmittance, offers detailed insights into the structural composition at the nano level. Structural characterization involves techniques such as XRD, Energy dispersive X-ray (EDX), XPS, IR, Raman, BET, and Zieta size analyzer.

SEM, TEM, XRD, AFM, and Dynamic Light Scattering (DLS) can be used to estimate particle size, with DLS being effective in liquid media. Optical characterization techniques, including UV-Vis, Photoluminescence (PL), and Ellipsometer, reveal the optical properties, crucial for applications like photocatalysis. BET is the preferred technique for determining surface area. These techniques collectively provide a comprehensive understanding of the physicochemical, morphological, structural, particle size, and optical properties of nanoparticles. [10]

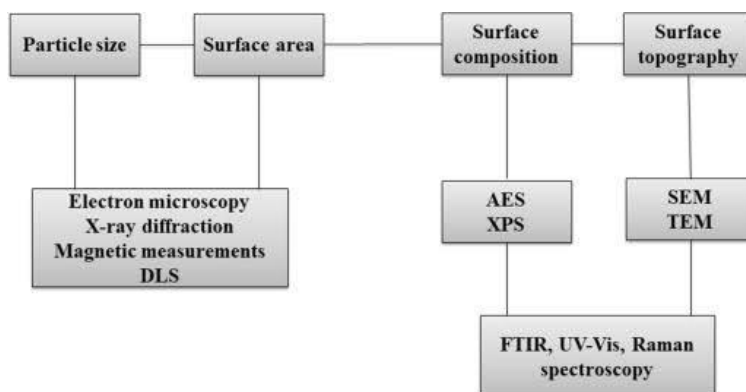


Fig-3. Characteristics of Nanoparticles. [11]

I.1.4 Applications of Nanoparticles:

Nanoparticles (NPs) exhibit diverse applications :

- *Drug Delivery*: Enhances drug effectiveness with reduced side effects, utilizing iron oxide, gold, and silica-gold NPs.
- *Manufacturing and Materials*: Impacts various industries, including microelectronics and aerospace, with applications in chemical and biosensors.
- *Environmental Use*: Addresses eco-toxicity, removes heavy metals from water, and aids in photo degradation for environmentally friendly products.
- *Electronics*: Enables printed electronics using metallic and organic electronic NPs, offering low-cost, large-area solutions.
- *Energy Harvesting*: Plays a vital role in renewable energy sources, utilizing NPs for water splitting, energy storage, and nanogenerators.

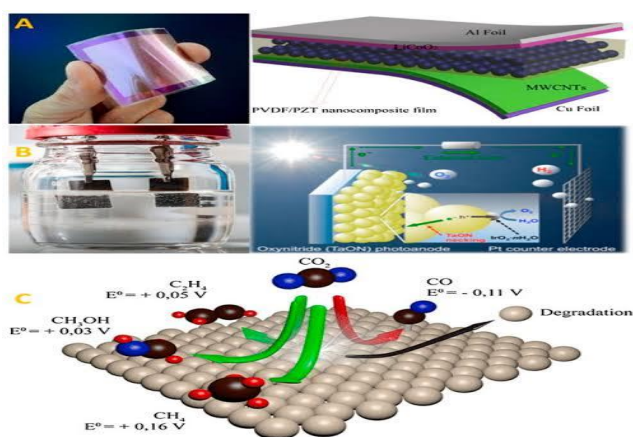


Fig- 4. Energy generation approaches from (A) Piezoelectrics actuators (B) Water splitting (C) CO₂ reduction.

- *Mechanical Industries:* Enhances mechanical strengths in coatings, lubricants, and adhesives, controlling tribological properties at the nanoscale. [12]

I.2 Plasma:

I.2.1 Definition:

Plasma is an extremely hot substance consisting of ionized gas, forming stars and appearing in lightning and neon signs. Scientists refer to it as the "fourth state of matter," and it is utilized in fields such as fusion energy, computer manufacturing, rocket propulsion, environmental cleanup, and advanced applications. [13]

In the field of physics, plasma is considered an ionized gas obtained by stimulating it through heat, radiation, or electrical current. Plasma is recognized as the fourth state of matter, distinguished by its rapid overall response. Interactions occur as electrons generated collide with gas particles and atoms, leading to ionization. Plasma contains charged particles, radicals, and excited molecules, generating ultraviolet rays and a traversing electric field.

Recent developments in plasma technology have led to the production of non-thermal plasma, formed at atmospheric pressure and room temperature. This differs from thermal plasma used in electric welding, ion thrusters, or tissue cutting, which relies on high temperatures. In non-thermal plasma, therapeutic effects are primarily influenced by the molecular species present, with tissues demonstrating better tolerance to treatment.

To generate cold plasma, an electrical current is applied using a high-voltage generator, such as the dielectric barrier discharge (DBD) technique. Various sources, including plasma guns, can produce cold plasma by exciting a rare gas (e.g., helium or neon) through an electric current. The plasma travels over significant distances to the targeted treatment area. Local application and gas variety are utilized to adjust the desired properties of the plasma. [14]

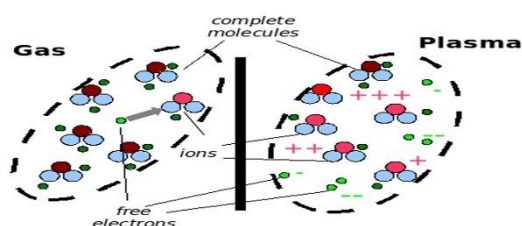


Fig-5. The difference between plasma and gas. [15]

I.2.2 Structure and composition of plasma:

In the context of the synthesis of ZnO nanoparticles by cold plasma, it is important to understand in detail the structure and composition of the plasma used for this method. Plasma is created by the application of external energy to a gas, which can be atmospheric air, helium, argon or oxygen, among others. This energy ionizes the atoms and molecules of the gas, creating a mixture of charged and neutral particles. [16]

The plasma structure can vary depending on several factors, such as the nature of the original gas, the applied power density, and the pressure and temperature conditions. Depending on these factors, several regions in the plasma can be distinguished, such as the cold plasma region, where charged particles are few in number and neutral species dominate, or the hot plasma region, where the electron and ionic density are high and the temperature is high. [17]

The composition of the plasma can also vary depending on the formation conditions and the nature of the gases used. Species present in plasma can include ions, electrons, neutral atoms, molecules, radicals and photons, among others. Charged species, such as ions and electrons, are often the most important species for cold plasma nanoparticle synthesis processes because they are responsible for generating the energy necessary for nanoparticle formation. [15]

I.2.3 Properties of plasma:

The properties of plasma are closely related to its structure and composition, and these properties have a great influence on the synthesis of ZnO nanoparticles by cold plasma. An important property of plasma is its electrical conductivity, which is due to the presence of free electrons and ions in the plasma. This conductivity can be controlled by the applied power density and the composition of the gas used, which makes it possible to modify the properties of the plasma to optimize the synthesis of ZnO nanoparticles. [18]

Another important property is the plasma temperature, which can vary from a few thousand to tens of thousands of degrees Celsius depending on the formation conditions. This high temperature makes it possible to activate specific chemical reactions for the synthesis of ZnO nanoparticles.

Besides the temperature, the electron and ionic density of the plasma can also be modified to optimize the synthesis of ZnO nanoparticles. High electron densities can be used to ionize ZnO precursors, while high ion densities can be used to form ZnO nanoparticles. [19]

Other plasma properties may also play an important role in cold plasma synthesis of ZnO nanoparticles, such as retention time, pressure, and gas flow rate. By modifying these properties, it is possible to control the formation, size and shape of ZnO nanoparticles. [20]

I.2.4 Plasma Generation Techniques

- **DC Glow Discharge:** This falls under non-thermal plasma, where a Direct Current (DC) electric source is connected between the cathode and anode plates, and the application of plasma gas is carried out between the plates for plasma generation.

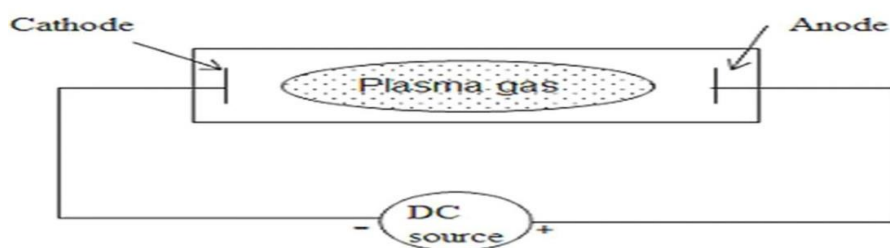


Fig-6. System for DC glow discharge

The application of a direct current (DC) electric field between the cathode and anode plates accelerates electrons, increasing inelastic collisions between atoms and electrons, leading to ionization and excitation. Newly created ions and electrons are strongly accelerated towards the cathode, discharging new electrons through ionization-induced secondary electron emission. The increased ionization collisions enhance the formation of self-sustaining plasma glow. This can be widely used in material processing, as a light source, in etching, ion deposition, and as a physical mechanism for surface modification.

- Radio Frequency Discharge:** Plasma is generated by either stimulating interaction or current induction within the radio frequency range (1 kHz to 103 MHz), with power supplied by alternating current. There are two types of radio frequency plasma discharge: Capacitive Coupled Discharge (CCD) and Inductively Coupled Discharge (ICD). In the capacitive coupled discharge system, electrodes are powered through a capacitor by an alternating current voltage source, while the other electrode remains solidly grounded. The capacitor charges rapidly during the positive half of the voltage source, causing a voltage drop across the plasma. Charging of the capacitor by ion current and plasma voltage drop likely occurs in the negative half cycle, but the voltage remains predominant due to lower ion mobility. Widely used as a medium for low-temperature plasma processing of materials in aerospace and microelectronics fields.

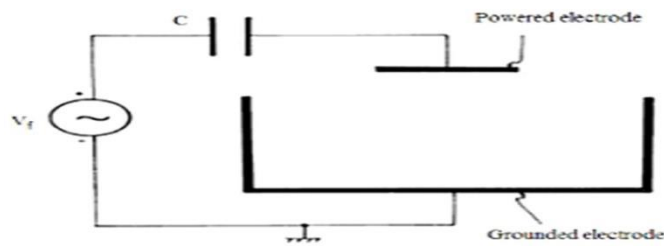


Fig-7. Capacitive coupled discharge system

The inductively coupled discharge involves the configuration of cylindrical helical coils, where magnetic induction generates electric current. Passing current through the coils creates a time-varying magnetic flux, inducing a thin electric field that sustains plasma discharge and accelerates free electrons.

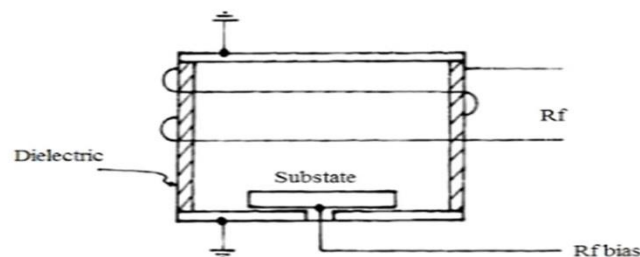


Fig-8. Inductively coupled discharge system

Transformer coupling often helps create an electromagnetic field between the induction coils and plasma in the frequency range of 1 to 100 MHz. It is highly efficient in generating oscillations and accelerating electrons in curved orbits, significantly reducing electron losses with the walls. It is preferred for use in deposition and etching processes for treating semiconductor wafers and modifying the surfaces of diamond films for manufacturing purposes.

- Hydrogen Production from Alcohols:** Non-thermal plasma has more applications in the industry compared to thermal plasma. Methanol boasts a high hydrogen-to-carbon ratio and can be produced abundantly from methane. Conversion of methanol to hydrogen can be achieved using Dielectric Barrier Discharge (DBD) plasma, corona discharge plasma, surface-wave discharge plasma, microwave plasma, glow discharge plasma, pulse charge plasma, etc. DBD is also known as silent plasma. Plasma is generated by utilizing two electrodes with a barrier between them made of a dielectric material of a few millimeters in thickness. Three different variants of the setup used for creating DBD plasma are shown. [17]

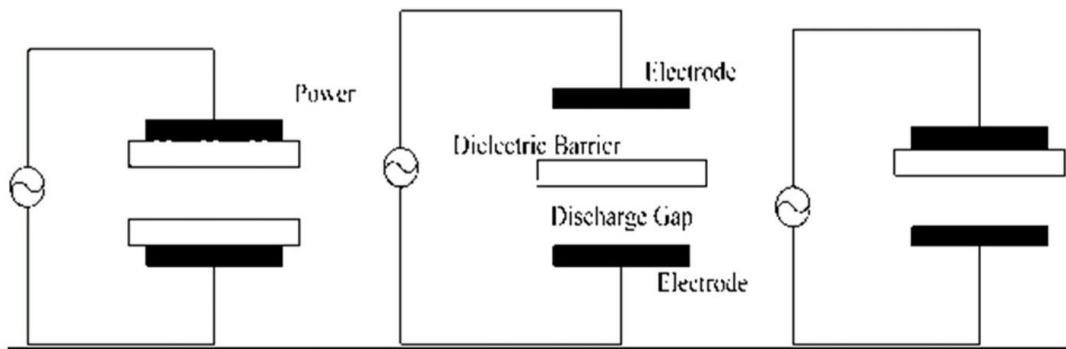


Fig-9. Three basic configurations

I.2.5 Applications of plasma:

- Pollution Treatment:** Non-thermal Plasma is used to reduce NO_x emissions in diesel engines by reacting with free electrons, ions, and radicals.
- Liquid Radioactive Waste Utilization:** Plasma technology aids in the utilization and neutralization of liquid radioactive waste in the nuclear fuel cycle.

- **Semiconductor Processing:** Plasma enables the production of silicon wafers for semiconductor chips, with applications in etching and ion implantation.
- **Living Tissues Treatment:** Cold Plasma treatment is utilized in biomedical applications, ensuring selectivity, reduced invasiveness, and avoidance of thermal effects.
- **High Energy Density Pinch Plasma:** Low-temperature plasmas are preferred for nanotechnology applications due to their characteristics and energy efficiency.
- **Plasma Pencil:** Used in medical fields for wound healing, bacteria elimination, and surface modification of heat-sensitive materials using low-pressure plasma.
- **Low Current Non-Thermal Plasma Tron:** Efficiently produces hydrogen gas for various industrial uses, providing a cost-effective and energy-efficient alternative.
- **Treatment of Prostate Cancer:** Low-temperature Atmospheric Plasma is employed to break down DNA double strands in prostate cancer cells, offering a low side-effect treatment.
- **Plasma Cutting:** Plasma is used for cutting materials, showing significant improvements in the cutting system, especially for stainless steel, mild steel, and aluminum.
- **Plasma Etching:** Applied in silicon dioxide for memory devices, utilizing various gases like SF₆ and CF₄ for chemical etches.
- **Surface Treatment:** Techniques like Glow Discharge Cleaning and Plasma Immersion Ion Implantation harden surfaces, improving wear resistance.
- **Plasma Antenna for Beam Forming:** Used in communication and radio detection, with applications in effective radiation and targeted electromagnetic wave reflection.
- **Atmospheric Pressure Plasma Jet:** Overcomes the limitations of vacuum systems, providing efficient material processing at low temperatures using helium flow and a unique electrode design.

- **Plasma Gun Techniques for Fusion:** Involves Plasma Flow Switch and coaxial guns to generate fusion temperature Plasma, contributing to controlled fusion research.
- **Plasma Ion Implantation and Deposition:** Techniques like PBII and PBIID are used for treating objects in a three-dimensional manner, finding applications in tribology and microelectronics.
- **Electro thermal and Electromagnetic Plasma for Surface Treatment:** Launchers producing hot, dense Plasma are used for coating surfaces, enhancing material properties and corrosion resistance. [21]

References I :

- [1] G. S. Bilotta and R. E. J. W. r. Brazier, "Understanding the influence of suspended solids on water quality and aquatic biota," vol. 42, no. 12, pp. 2849-2861, 2008.
- [2] W. Gwenzi, N. Chaukura, C. Noubactep, and F. N. J. J. o. e. m. Mukome, "Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision," vol. 197, pp. 732-749, 2017.
- [3] Q. Qiu Zhao, A. Boxman, and U. J. J. o. N. R. Chowdhry, "Nanotechnology in the chemical industry—opportunities and challenges," vol. 5, pp. 567-572, 2003.
- [4] M. Ansari, G. Moussavi, M. H. Ehrampoosh, and S. J. J. o. W. P. E. Giannakis, "A systematic review of non-thermal plasma (NTP) technologies for synthetic organic pollutants (SOPs) removal from water: Recent advances in energy yield aspects as their key limiting factor," vol. 51, p. 103371, 2023.
- [5] J. K. Patel, A. Patel, and D. Bhatia, "Introduction to nanomaterials and nanotechnology," in *Emerging technologies for nanoparticle manufacturing*: Springer, 2021, pp. 3-23.
- [6] B. Rozenberg and R. J. P. i. p. s. Tenne, "Polymer-assisted fabrication of nanoparticles and nanocomposites," vol. 33, no. 1, pp. 40-112, 2008.
- [7] M. A. Ahmadi-Pajouh, T. S. Ala, F. Zamanian, H. Namazi, and S. J. F. Jafari, "Fractal-based classification of human brain response to living and non-living visual stimuli," vol. 26, no. 05, p. 1850069, 2018.
- [8] S. A. M. Ealia and M. P. Saravanakumar, "A review on the classification, characterisation, synthesis of nanoparticles and their application," in *IOP conference series: materials science and engineering*, 2017, vol. 263, no. 3, p. 032019: IOP Publishing.
- [9] J. Jeevanandam, A. Barhoum, Y. S. Chan, A. Dufresne, and M. K. J. B. j. o. n. Danquah, "Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations," vol. 9, no. 1, pp. 1050-1074, 2018.
- [10] S. Mourdikoudis, R. M. Pallares, and N. T. J. N. Thanh, "Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties," vol. 10, no. 27, pp. 12871-12934, 2018.
- [11] M. Sajid and J. J. M. J. Płotka-Wasyłka, "Nanoparticles: Synthesis, characteristics, and applications in analytical and other sciences," vol. 154, p. 104623, 2020.
- [12] I. Khan, K. Saeed, and I. J. A. j. o. c. Khan, "Nanoparticles: Properties, applications and toxicities," vol. 12, no. 7, pp. 908-931, 2019.
- [13] A. I. Morozov, *Introduction to plasma dynamics*. CRC Press, 2012.
- [14] A. Fridman, *Plasma chemistry*. Cambridge university press, 2008.
- [15] A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. J. I. t. o. p. s. Hicks, "The atmospheric-pressure plasma jet: a review and comparison to other plasma sources," vol. 26, no. 6, pp. 1685-1694, 1998.
- [16] U. R. Kortshagen, R. M. Sankaran, R. N. Pereira, S. L. Girshick, J. J. Wu, and E. S. J. C. r. Aydil, "Nonthermal plasma synthesis of nanocrystals: fundamental principles, materials, and applications," vol. 116, no. 18, pp. 11061-11127, 2016.
- [17] H. Conrads, M. J. P. s. s. Schmidt, and technology, "Plasma generation and plasma sources," vol. 9, no. 4, p. 441, 2000.
- [18] M. Buryi *et al.*, "Cold plasma treatment of ZnO: Er nano-and microrods: The effect on luminescence and defects creation," vol. 895, p. 162671, 2022.

- [19] M. Konuma, *Film deposition by plasma techniques*. Springer Science & Business Media, 2012.
- [20] Z. Luo, S. Tian, Z. J. I. Wang, and E. C. Research, "Enhanced activity of Cu/ZnO/C catalysts prepared by cold plasma for CO₂ hydrogenation to methanol," vol. 59, no. 13, pp. 5657-5663, 2020.
- [21] R. Jafari, S. Asadollahi, M. J. P. C. Farzaneh, and P. Processing, "Applications of plasma technology in development of superhydrophobic surfaces," vol. 33, pp. 177-200, 2013.



Chapter II

Synthesis of ZnO nanoparticles by cold plasma and their application

Introduction:

The synthesis of zinc oxide (ZnO) nanoparticles using cold plasma technology has gained considerable interest due to its ability to produce tailored nanoparticles with unique properties. Cold plasma offers precise control over synthesis parameters, resulting in uniform and scalable production of ZnO nanoparticles. These nanoparticles find applications in various fields, including electronics, medicine, and environmental remediation. In this review, we explore the synthesis of ZnO nanoparticles by cold plasma and their diverse range of applications.

II.1 Zinc oxide (ZnO) nanoparticles :**II.1.1 Synthesis of ZnO nanoparticles by cold plasma:**

The technique of generating zinc oxide nanoparticles through cold plasma is steadily advancing in the field of nanotechnology. This method allows for obtaining high-purity, small-sized nanoparticles with a narrow size distribution and well-defined surface. Additionally, it enables the production of highly stable nanoparticles that can be easily dispersed in water, making them valuable for use as antibacterial agents. The use of cold plasma as a synthesis method offers several advantages over traditional methods like solution synthesis. This approach does not require the use of harmful chemicals and provides precise control over the size and shape of nanoparticles. Moreover, it facilitates the synthesis of nanoparticles at relatively low temperatures, preventing the formation of undesirable phases. [1]

However, the synthesis of zinc oxide nanoparticles via cold plasma requires a deep understanding of the mechanisms involved in the process, including the atomic or molecular dissociation of zinc oxide precursors and their reassembly to form zinc oxide nanoparticles. Overall, the technology for generating zinc oxide nanoparticles through cold plasma holds promise for obtaining high-purity, small-sized nanoparticles with a narrow size distribution and well-defined surface. This method also offers precise control over the size and shape of nanoparticles while avoiding the use of harmful chemicals and the formation of unwanted phases. [2]

II.1.2 Principles of cold plasma synthesis:

Plasma techniques for manufacturing nano-sized zinc oxide particles offer exciting opportunities due to non-equilibrium thermal conditions, allowing chemical reactions at low temperatures. The use of strong discharges can also maintain high temperatures, supporting the formation of nano-sized particles. There are various methods to synthesize nano particles using plasma. Low-pressure plasma efficiently produces zinc oxide nanoparticles by maintaining uniform parameters. Electrical waves stimulate plasma discharge, loaded with reactive gases and precursors, forming and accumulating nanoparticles while preventing aggregation. High-quality nanoparticles result from surface reactions and elevated temperatures within the plasma. Atmospheric pressure plasma quickly heats radicals and charged particles, with low reactive species density. Plasma is sustained using low or high impedance discharges, with two devices depicted for zinc oxide nanoparticle production. Gas temperature inside the plasma column reaches about 10,000 Kelvin.

Zinc oxide nanoparticles improved surface adhesion via cold plasma treatment. Using dual barrier discharge (DBD), a nanoparticle film was formed, with some samples heated to create nanostructured zinc oxide walls. Low-frequency plasma discharge affected morphology, leading to complex compound formation with water vapor and reactive nitrogen species. Plasma treatment of liquid precursors synthesizes zinc oxide nanoparticles. Shuto et al. used continuous plasma over a zinc nitrate hexahydrate solution, forming nanostructures with potent shape-dependent antibacterial properties, inhibiting various bacteria. [3]

II.1.3 Parameters influencing the synthesis of nanoparticles:

Synthesis parameters significantly influence the size and morphology of ZnO nanoparticles produced by cold plasma. These parameters, such as the concentration of Zn^{2+} ions, plasma power, discharge time, gas flow rate, and substrate temperature, can be adjusted to control these characteristics. [4]

A higher concentration of Zn^{2+} ions can increase nanoparticle size, while increased plasma power can reduce it. Similarly, a longer discharge time can decrease nanoparticle size. Gas flow rate also plays a role, with an increase favoring size reduction. Additionally, a higher substrate temperature promotes particle growth. These parameters interact in a complex manner, requiring careful optimization to achieve the desired properties of ZnO nanoparticles. [5]

II.1.4 Characterization of ZnO nanoparticles:

The characterization of ZnO nanoparticles synthesized by cold plasma can be carried out using various techniques. [6] Using these characterization techniques, it is possible to determine the size, morphology, size distribution, purity, and crystalline quality of ZnO nanoparticles synthesized by cold plasma. This information is important for assessing the quality of ZnO nanoparticles and their suitability for use in various applications, [7] These are some of the most commonly used methods.

a. Transmission Electron Microscopy (TEM): This tool provides detailed visualization of the particles' external structure, estimates their size and shape, and offers insights into their crystalline structure. [8]

b. X-ray Diffraction (XRD): This technique is employed to determine the crystalline structure of particles and estimate their size using the Debye-Scherrer method.

c. X-ray Photoelectron Spectroscopy (XPS): This technique is used to analyze the chemical composition of particle surfaces and estimate their size based on electron penetration depth. [9]

d. Raman Scattering Spectroscopy: This technique is utilized to determine both the crystalline structure and chemical composition of ZnO nanoparticles. By identifying molecular vibrations within the nanoparticles, it aids in elucidating their crystalline structure and chemical composition. Moreover, Raman scattering spectroscopy can assess particle size by analyzing the relationship between particle size and the position of the Raman peak. [10]

e. Mass Spectrometry: This method is employed to ascertain the size and mass distribution of nanoparticles. Additionally, it facilitates the measurement of the

chemical composition of nanoparticles and the identification of chemical elements present within them. Through the application of these characterization techniques, researchers can acquire comprehensive insights into ZnO nanoparticles. This enables them to grasp their physical and chemical behaviors and optimize their synthesis for specific applications. [11]

f. UV-Vis Spectrometry: UV-vis spectroscopy is commonly utilized to explore the optical properties of ZnO nanoparticles. It enables the measurement of light absorption and reflection within the UV-visible range, offering information about the bandgap and electronic transition properties of nanoparticles. Photoluminescence is another method used to investigate light emission from ZnO nanoparticles upon excitation by a light source. [12]

g. FT-IR Spectrometry: Fourier Transform Infrared (FT-IR) spectrometry is a characterization technique employed for the analysis of ZnO nanoparticles. It identifies surface functional groups such as hydroxyl, carbonyl, and alkoxide groups, thereby providing insights into the chemical composition and interactions of nanoparticles. Furthermore, FT-IR spectrometry investigates surface modification processes and monitors changes in characteristic absorption bands. In summary, FT-IR spectrometry serves as a valuable tool for comprehending the structure, composition, and properties of ZnO nanoparticles. [13]

II.2 Wastewater Treatment:

II.2.1 Definition:

Wastewater treatment is considered a vital part of efforts to maintain water cleanliness and quality. The extensive use of water in industrial processes results in the generation of wastewater containing various pollutants. These pollutants include chemicals, organic substances, heavy metals, and others, which need to be effectively removed or reduced in concentration before the water is reused or discharged into the environment. [14]

II.2.2 Wast water pollutants:

Heavy metals: Heavy metals in wastewater pose a serious environmental problem, leading to harm to both the environment and human health, even at low concentrations. These metals do not easily break down and can cause health issues, such as cancer. They contribute to the deterioration of aquatic life and promote algae growth, and when discharged into rivers, they transform into hazardous ions. Therefore, removing heavy metals is essential to reduce environmental and health risks. [15]

Dyes: Dyes can be harmful to the environment and pollute water, with types such as basic and acidic dyes. Acidic dyes, used for coloring plastic products, are a concern due to their disposal challenges. Given the high demand for plastic products, large quantities of these dyes are produced, leading to significant waste generation. Various methods, including biological, physical, and chemical, are commonly used to treat such pollutants. [16]

Oils and petroleum derivatives: Water pollution from oils and petroleum derivatives is a serious environmental challenge. These substances are used in various industries and cause pollution when leaked from sources like oil tankers or industrial equipment. These materials form a layer on the water surface, hindering oxygen from reaching aquatic organisms and harming marine life and coastal plants. If water sources used for drinking or irrigation are contaminated with these substances, individuals may be poisoned. [17]

Industrial wastewater pollutants can be classified based on the industry sector. Each industry has its own specific types of pollutants. Below is a simplified table illustrating these classifications:

Pollutants	Sources
Suspended Particulate Matter, (SPM)	Automobile, power plants, boilers, Industries requiring crushing and grinding such as quarry, cement.
Chlorine	Sea-salt production, dechlorination, biomass burning and pulp & paper mills.
Fluoride	Fertilizer, aluminum refining.
Sulphur dioxide	Power plants, boilers, sulphuric acid manufacture, ore refining, petroleum refining.
Lead	Ore refining, battery manufacturing, automobiles.
Oxides of nitrogen, NO, NO ₂ (NOX)	Automobiles, power plants, nitric acid manufacture, also a secondary pollutant.
Peroxy acetyl nitrate, PAN	Secondary pollutant.
Formaldehyde	Secondary pollutant
Ozone	Secondary pollutant
Carbon monoxide combustion	Automobiles, incomplete fuel
Hydrogen sulphide	Pulp and paper, petroleum refining.
Hydrocarbons	Automobiles, petroleum refining
Ammonia	Fertilizer plant, degradation of dead animals.

Table-1. Pollutants and its Sources. [18]

II.2.3 Different methods for treating industrial wastewater:

Advancements in wastewater treatment aim to meet clean water standards, but effective treatment remains a challenge. Various methods are used with different pros and cons, and selection depends on cost and treatment efficiency. [19]

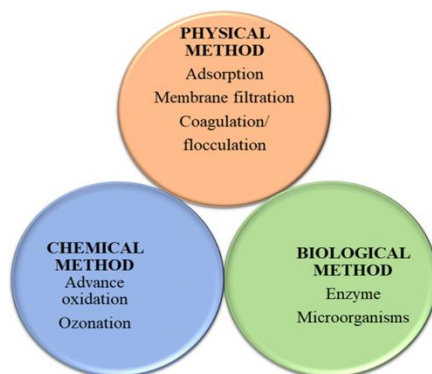


Fig-10. Conventional and advanced techniques used for wastewater treatment. [20]

II.2.3.1 Physical methods: Mass transfer strategy is the foundation of physical pollutant removal methods, preferred for its simplicity, high efficiency, and minimal chemical usage. Physical treatment is considered more reliable than other methods and includes the use of adsorption due to its high efficiency and low cost. [21]

II.2.3.2 Adsorption: Adsorption is an effective and reliable method for wastewater treatment, where dissolved compounds are transferred from the liquid phase to a solid surface. The removal efficiency of adsorption can reach up to 99.9%. considers adsorption as one of the best treatment technologies. [22]

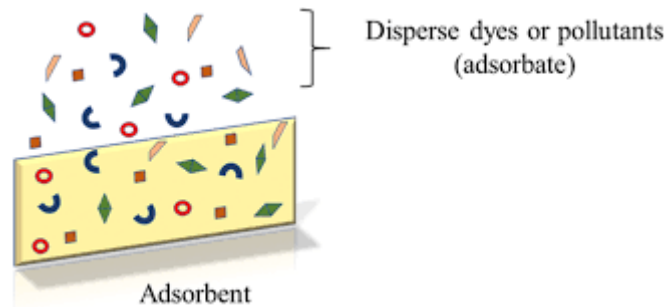


Fig-11. General mechanism of adsorption to remove contaminants

II.2.3.3 Membrane Filtration: Membrane filtration is one of the most effective wastewater treatment techniques, but developing a membrane with thermal stability and improved performance remains a challenge. The hydrophilicity and surface charge of the membrane affect its performance, and the general mechanism of membrane filtration is shown in Figure 12. [23]

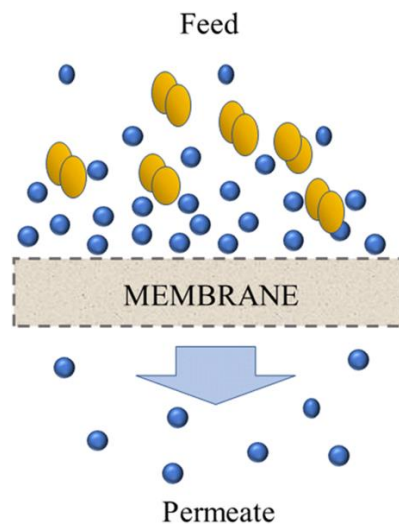


Fig-12. General mechanism of membrane filtration to remove contaminants.

II.2.3.4 Chemical method:

Chemical oxidation processes used in catalysis applications, such as AOPs, are reported for wastewater treatment and generating hydroxyl radicals. These processes include electrochemical oxidation, photo-electrochemical oxidation, Fenton's oxidation, and ozonation. Catalysts and pH play a crucial role in these processes. [24]

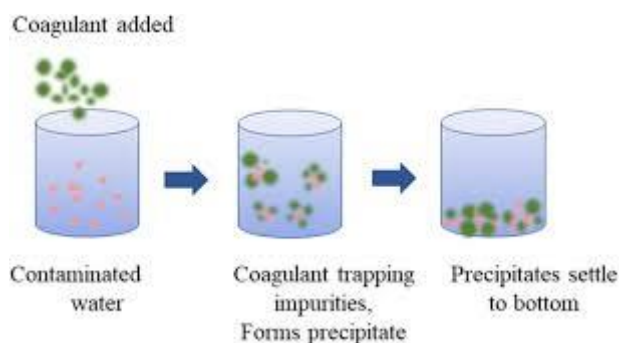


Fig- 13. General mechanism of coagulation/flocculation to remove contaminants. [25]

II.2.3.5 Electrochemical oxidation: Advanced electrochemical oxidation processes (EAOPs) are effective for pollutant removal in an environmentally friendly manner, but energy cost is the main challenge. Electrode materials have been improved to enhance efficiency. Using pulse current in electrochemical oxidation reduces energy consumption. A study on wastewater treatment using electrochemical oxidation showed energy savings. [26]

II.2.3.6 Photo-electrochemical oxidation: To remove and degrade pollutants, advanced oxidation processes (AOPs) based on hydroxyl radicals ($\bullet\text{OH}$) are essential. In photo-electrocatalysis, solar light is used for dye removal. $\bullet\text{OH}$ radicals enhance removal efficiency and reduce dye concentrations in wastewater. [27]

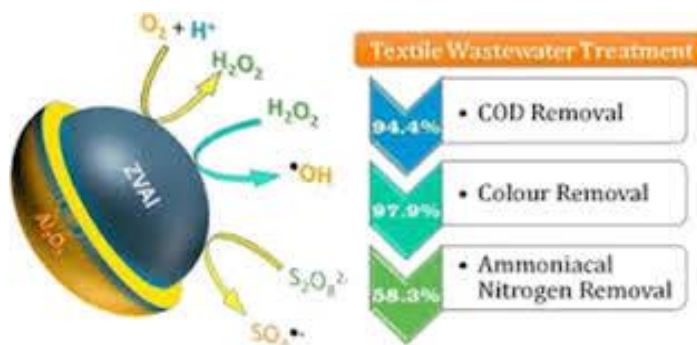


Fig- 14. Textile wastewater treatment by advanced oxidation process. [28]

II.2.3.7 Fenton's oxidation: Advanced oxidation processes (AOPs) are used for the degradation of organic compounds and dyes in industrial wastewater. Fenton's oxidation is an effective method that uses ferrous sulfate and hydrogen peroxide to produce hydroxyl radicals, and it has been successfully employed for industrial wastewater treatment. The reactions involve the generation of hydroxyl radicals when hydrogen peroxidaton interacts with iron ions. [29]

II.2.3.8 Biological method:

Microorganisms break down organic dyes in wastewater treatment, but textile dyes require special treatment. Biological processes are environmentally friendly and cost-effective compared to physical methods, but they may be insufficient for some dyes and require longer time. [30]

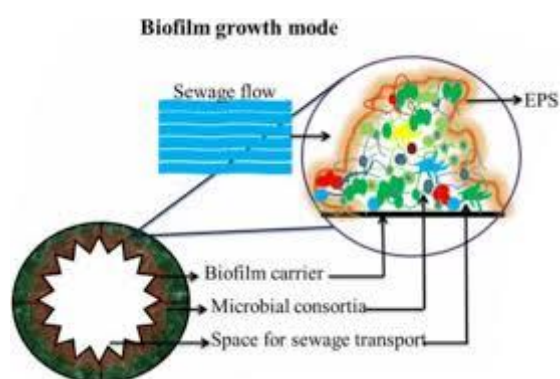


Fig- 15. Biofilm for sewage water treatment. [31]

References III :

- [1] A. Roy and J. Bhattacharya, *Nanotechnology in industrial wastewater treatment*. IWA Publishing, 2015.
- [2] A. K. Mandal *et al.*, "Current research on zinc oxide nanoparticles: Synthesis, characterization, and biomedical applications," vol. 12, no. 17, p. 3066, 2022.
- [3] K. Kim and T. J. J. o. A. P. Kim, "Nanofabrication by thermal plasma jets: From nanoparticles to low-dimensional nanomaterials," vol. 125, no. 7, 2019.
- [4] B. M. SHAIBU, "PREPARATION AND CHARACTERISATION OF PLANTAIN WASTE BASED CELLULOSIC NANOCOMPOSITES FOR THE REMOVAL OF SELECTED HEAVY METALS FROM BATTERY EFFLUENT," 2021.
- [5] Z. Xing *et al.*, "Highly reversible zinc-ion battery enabled by suppressing vanadium dissolution through inorganic Zn²⁺ conductor electrolyte," vol. 90, p. 106621, 2021.
- [6] G. Primc, K. Brenčič, M. Mozetič, and M. J. N. Gorjanc, "Recent advances in the plasma-assisted synthesis of zinc oxide nanoparticles," vol. 11, no. 5, p. 1191, 2021.
- [7] R. Manjunatha, K. Usharani, D. J. J. o. P. Naik, and Phytochemistry, "Synthesis and characterization of ZnO nanoparticles: A review," vol. 8, no. 3, pp. 1095-1101, 2019.
- [8] C. Mühlfeld *et al.*, "Visualization and quantitative analysis of nanoparticles in the respiratory tract by transmission electron microscopy," vol. 4, pp. 1-17, 2007.
- [9] S. Wolter, B. Luther, D. Waltemyer, C. Önnby, S. E. Mohny, and R. J. A. P. L. Molnar, "X-ray photoelectron spectroscopy and x-ray diffraction study of the thermal oxide on gallium nitride," vol. 70, no. 16, pp. 2156-2158, 1997.
- [10] A. Sahai, N. J. P. E. L.-d. S. Goswami, and Nanostructures, "Structural and vibrational properties of ZnO nanoparticles synthesized by the chemical precipitation method," vol. 58, pp. 130-137, 2014.
- [11] H. E. Pace, N. J. Rogers, C. Jarolimek, V. A. Coleman, C. P. Higgins, and J. F. J. A. c. Ranville, "Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry," vol. 83, no. 24, pp. 9361-9369, 2011.
- [12] S. Jurablu, M. Farahmandjou, and T. J. J. o. S. Firoozabadi, Islamic Republic of Iran, "Sol-gel synthesis of zinc oxide (ZnO) nanoparticles: study of structural and optical properties," vol. 26, no. 3, pp. 281-285, 2015.
- [13] N. M. Shamhari, B. S. Wee, S. F. Chin, and K. Y. J. A. C. S. Kok, "Synthesis and Characterization of Zinc Oxide Nanoparticles with Small Particle Size Distribution," vol. 65, no. 3, 2018.
- [14] H. Mohammadi, "Improvement Strategy for reducing environmental impact of a wastewater treatment plant," PAUWES, 2020.
- [15] S. Mishra *et al.*, "Heavy metal contamination: an alarming threat to environment and human health," pp. 103-125, 2019.
- [16] R. Al-Tohamy *et al.*, "A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety," vol. 231, p. 113160, 2022.
- [17] D. J. C. Reis, *Environmental control in petroleum engineering*. Elsevier, 1996.
- [18] J. Singh, P. Yadav, A. K. Pal, and V. J. S. i. w. p. m. R. o. m. Mishra, "Water pollutants: Origin and status," pp. 5-20, 2020.

- [19] A. Saravanan *et al.*, "Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development," vol. 280, p. 130595, 2021.
- [20] J. O. Eniola, R. Kumar, M. Barakat, and J. J. J. o. C. P. Rashid, "A review on conventional and advanced hybrid technologies for pharmaceutical wastewater treatment," vol. 356, p. 131826, 2022.
- [21] V. Augugliaro, M. Litter, L. Palmisano, J. J. J. o. p. Soria, and p. C. P. reviews, "The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance," vol. 7, no. 4, pp. 127-144, 2006.
- [22] M. N. J. O. p.-m. Rashed, risk and treatment, "Adsorption technique for the removal of organic pollutants from water and wastewater," vol. 7, pp. 167-194, 2013.
- [23] A. I. Schäfer, I. Akanyeti, A. J. J. A. i. c. Semião, and i. science, "Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens," vol. 164, no. 1-2, pp. 100-117, 2011.
- [24] J. L. Wang, L. J. J. C. r. i. e. s. Xu, and technology, "Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application," vol. 42, no. 3, pp. 251-325, 2012.
- [25] E. López-Maldonado, M. Oropeza-Guzman, J. Jurado-Baizaval, and A. J. J. o. h. m. Ochoa-Terán, "Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements," vol. 279, pp. 1-10, 2014.
- [26] O. Ganzenko, D. Huguenot, E. D. Van Hullebusch, G. Esposito, M. A. J. E. S. Oturan, and P. Research, "Electrochemical advanced oxidation and biological processes for wastewater treatment: a review of the combined approaches," vol. 21, pp. 8493-8524, 2014.
- [27] J. D. García-Espinoza, I. Robles, A. Durán-Moreno, and L. A. J. C. Godínez, "Photo-assisted electrochemical advanced oxidation processes for the disinfection of aqueous solutions: A review," vol. 274, p. 129957, 2021.
- [28] S. Hutagalung, I. Muchlis, and K. Khotimah, "Textile wastewater treatment using advanced oxidation process (AOP)," in *IOP conference series: materials science and engineering*, 2020, vol. 722, no. 1, p. 012032: IOP Publishing.
- [29] A. S. J. G. N. j. Stasinakis, "Use of selected advanced oxidation processes (AOPs) for wastewater treatment—a mini review," vol. 10, no. 3, pp. 376-385, 2008.
- [30] D. Bhatia, N. R. Sharma, J. Singh, R. S. J. C. R. i. E. S. Kanwar, and Technology, "Biological methods for textile dye removal from wastewater: A review," vol. 47, no. 19, pp. 1836-1876, 2017.
- [31] M. C. Van Loosdrecht and S. J. J. T. i. b. Heijnen, "Biofilm bioreactors for waste-water treatment," vol. 11, no. 4, pp. 117-121, 1993.





Chapter I

Materials and methods

Introduction:

Nanotechnology is a revolution in our modern life, enhancing the efficacy of medical treatments, electronics performance, and renewable energy technologies thanks to small structures with unique properties, designed and engineered at the atomic and molecular levels. [1]

Therefore, harnessing nanoparticles has unlocked a world of possibilities for researchers and innovators to develop new materials. Zinc oxide stands out as one of the most remarkable nanomaterials due to its unique combination of properties, including high transparency and a wide band gap. [2]

These properties make them ideal for optoelectronic devices such as solar cells, sensors, and light-emitting diodes (LEDs). Additionally, their remarkable catalytic properties make them useful in chemical synthesis applications, particularly in environmental remediation, where they have been reported to remove heavy metals, organic compounds, and even microorganisms through adsorption or photocatalytic degradation. [3]

The use of GAD plasma technology in synthesizing zinc oxide nanoparticles is an innovative step, offering several advantages such as utilizing air as a source gas and generating a high concentration of active particles. These particles hold significant potential for various applications such as photocatalytic degradation of pollutants, advanced electronics, and drug delivery in biomedicine. The aim of this study is to explore the capability of GAD plasma technology in synthesizing zinc oxide nanoparticles and characterizing their physical and chemical properties, as well as testing their photocatalytic activity against specific pollutants to evaluate their effectiveness in wastewater treatment.

I.1. Material:

Analytical chemicals were used without additional purification. High purity zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and MB($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) (319.85 g/mol) were purchased from Sigma-Aldrich. Distilled water was used to prepare ZnO NPs sample.

I.2. Methods:

I.2.1. Synthesis of ZnO nanoparticles by cold plasma:

We dissolve 20 g of zinc acetate in 1000 ml of distilled water, then put it on a magnetic mixer until it becomes homogeneous with each other for 15 minutes, then 100 ml is poured into a thermal reactor cooled to water at a distance of approximately 5 cm from the ends of the electrodes, while magnetically stirring the solution and exposing it to plasma for 15 minutes.

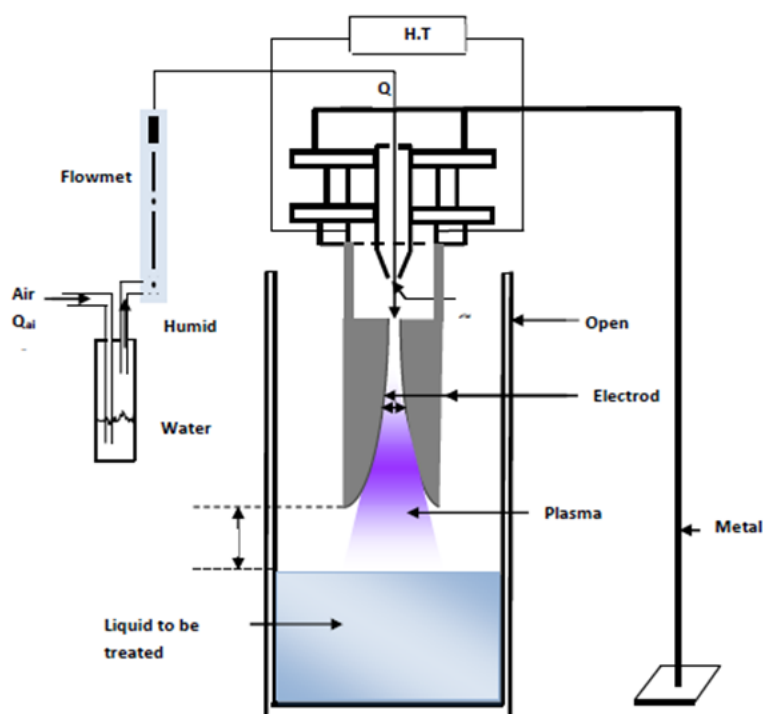


Fig-16.Schematic of the gliding arc discharge reactor. [4]

After stopping the discharge, the exposed solution is placed on a hot plate under stirring to dry. When the drying is finished, we carry out the pelleting process, thus we obtain a powder which is placed in an oven at 700°C for 4 hours.

Then we take it out of the oven and grind it well, and that's how we get zinc oxide nanoparticles.



Fig-17. The synthesized nanoparticle powder.

I.2.2. Characterizations:

Powder XRD data were obtained using a Proto AXRD-2 diffractometer with sample spinner and a Dectris My then 1K (3.22° active length*) 1D-detector in Bragg–Brentano geometry with a Copper Line Focus x-ray tube and Ni $k\beta$ absorber. The Thermo Scientific TM Quattro SEM combines all-around imaging and analytics performance with an innovative environmental mode (ESEM) that allows materials to be examined in their natural condition. The powder samples' optical characteristics were measured using a Shimadzu 3101PC double-beam spectrophotometer. The spectrophotometer (Shimadzu model IR I Raffinity-1) measured FTIR absorption in the spectral region $400\text{--}4000\text{ cm}^{-1}$. To discover the photocatalytic activity of the NPs, the Shimadzu Spectrophotometer UV-1800 was employed. METTLER TOLEDO's Simultaneous Thermal Analysis Device (TGA/DSC): TGA/DSC 3+1600 °C has been used to track changes in mass and thermal flow as a function of temperature. It allows users to evaluate a wide range of samples. The ability to conduct analyses in a controlled environment at temperatures ranging from 25 to 1600°C (air, nitrogen or argon). Heater rate: 0.1 to 100 °C min⁻¹. Balance: 5 g measurement range with 1 µg creams available: aluminum and platinum creams (70 µl) and huge aluminum creams (600 and 900 µl). LUXMETER 400,000 LUX - USB used for measuring sunlight intensity.

I.2.3. Photocatalytic activity:

I.2.3.1 Under Sunlight:

Before photocatalysis, the dispersion was continuously stirred in the dark room for 30 min to allow the reaction. The dye molecules and the catalyst surface to reach an equilibrium state between adsorption and desorption.

After stirring the dispersant for 30 minutes, it is exposed to sunlight for 90 minutes. Every 15 minutes, the beaker It was removed, and 4 mL was centrifuged to separate the suspensions of ZnO nanoparticles (NPs) from the solution.

Sample (100 ml) of dye (MB solution) at initial concentration 7 ppm was mixed with 100 mg of prepared ZnO in an open beaker (250 ml) used as a photoreactor. the dye concentration was determined using a UV-visible spectrophotometer at wavelengths of 663 nm Samples were taken at the specified time, centrifuged, and the dye concentrated it was measured at 663 nm. Using the following formula (Equation 1), the rate of degradation was determined.

$$\% \text{ Deg} = 100 \times \frac{A_0 - A_t}{A_0} \quad (1)$$

- Where A_t represents the absorbance of the dye at time t and A_0 represents the initial absorbance.

I.2.3.2 Under plasma:

100 ml of methylene blue solution is exposed to plasma for 90 minutes. Every 15 minutes, 4 ml are taken and placed in a tube, and then the various concentrations of all samples are measured using a UV-visible spectrophotometer at wavelength of 663nm.

In the second part of the experiment, the homogeneous mixture consisting of 100 ml of the aforementioned organic dye solution with 100 mg of catalyst is exposed under cold plasma for 90 min. Every 5min, the beaker It was removed, and 4 mL was centrifuged to separate the suspensions of ZnO nanoparticles (NPs) from the solution.

The dye concentration was determined using a UV-visible spectrophotometer at wavelengths of 663 nm Samples were taken at the specified time, centrifuged, and the dye concentrated it was measured at 663 nm. Using the following formula (Equation1), the rate of degradation was determined.

References 36:

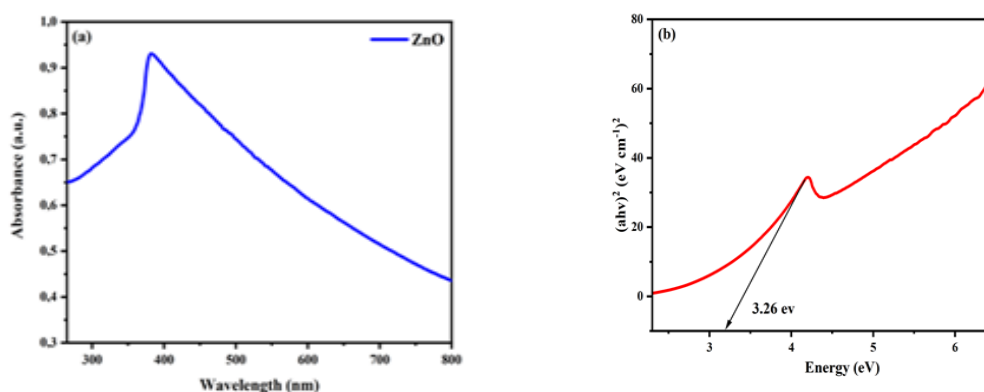
- [1] S. Malik, K. Muhammad, and Y. J. M. Waheed, "Nanotechnology: A revolution in modern industry," vol. 28, no. 2, p. 661, 2023.
- [2] P. J. A. J. A. B. S. Walia, "Synthesis and structural properties of zinc oxide nano particles (ZnO NPs): a review," vol. 2 ,pp. 39-49, 2014.
- [3] M. S. AlSalhi, J. Alam, L. A. Dass, and M. J. I. J. o. M. S. Raja, "Recent advances in conjugated polymers for light emitting devices," vol. 12, no. 3, pp. 2036-2054, 2011.
- [4] G. Zhao *et al.*, "Rotating gliding arc plasma: Innovative treatment for adhesion improvement between stainless steel heating elements and thermoplastics in resistance welding of composites," vol. 272, p. 111210, 2024.



II.1 Characteristics of the synthesized ZnO:

II.1.1 UV-visible study:

Zinc oxide is a semiconductor material characterized by a bandgap of 3.28 electron volts, and this value varies depending on multiple factors such as crystal structure, particle size, and shape. The UV-visible spectrum clearly shows the absorption of synthesized zinc oxide particles, with an approximate optical bandgap of 3.26 electron volts. The bandgap affects the electrical, optical, and catalytic properties of the particles, and reducing the bandgap can improve electrical conductivity, which is crucial for applications like transparent conductive films and solar cells. The bandgap also plays a significant role in determining the oxidative and catalytic properties of zinc oxide, as the particle surfaces catalyze a variety of chemical reactions.

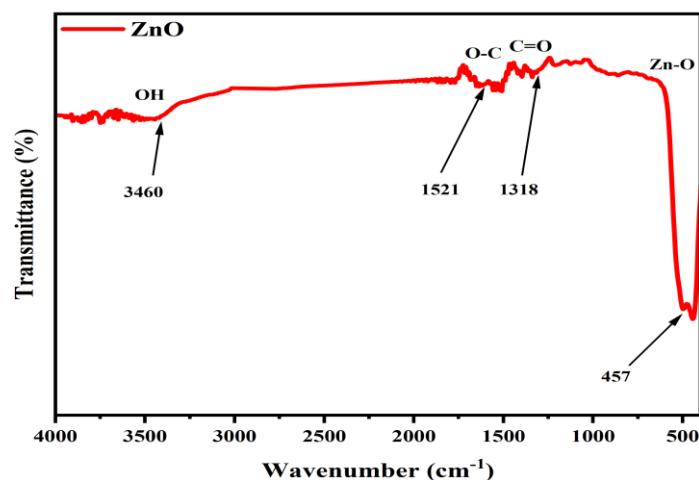


Cur-1. (a) Plot of $(\alpha h\nu)^2$ versus photon energy of synthesized ZnO. (b) Inset shows the Urbach energy plot of $\ln(\alpha)$ versus $(h\nu)$

II.1.2 FTIR Spectroscopic Analysis:

FTIR analysis is utilized to identify the functional groups in zinc oxide particles. The spectrum of zinc acetate solution treated with non-thermal plasma (GAD) before and after heating at 600°C for 3 hours is depicted in Cur-2. The peak positions observed in the FTIR spectrum and their functional origins are presented. As a result of plasma treatment of zinc acetate solution, the FTIR spectrum before heating reveals several absorptions (457, 1318, 1521, and 3460 cm⁻¹) corresponding to organic functional groups. The peaks at 1318 and 1521 cm⁻¹ are attributed to the asymmetric stretching vibrations of (C=O) and (O-C) bonds, respectively. Following heating, the FTIR

spectrum of zinc oxide particles exhibits a sharp peak at 457 cm^{-1} associated with Zn-O vibration and a broad peak at 3460 cm^{-1} related to O-H bonding due to moisture absorption.

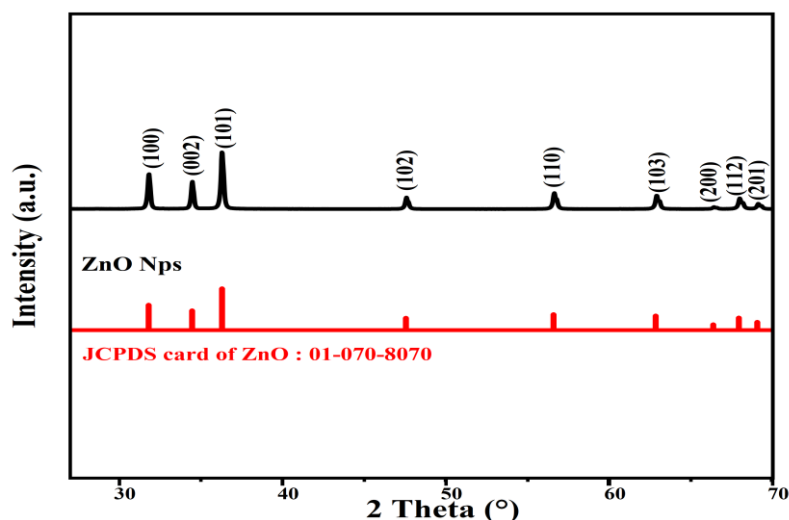


Cur-2. FTIR spectra of ZnO NPs and inset shows the enlarged spectra in the range $<600 \text{ cm}^{-1}$.

II.1.3 X-ray diffraction:

X-ray diffraction (XRD) was utilized to investigate the structure and composition of zinc oxide particles, with the results displayed in Cur-3. It was observed that numerous peaks corresponded to the crystalline surfaces of zinc oxide such as (100), (002), (101), (102), (110), and (103), indicating a hexagonal crystalline structure.

The sample under study comprised small particles, confirmed by the XRD data. The single crystal phase of zinc oxide was determined through the diffraction pattern, revealing that the (101) surface represents a hexagonal crystal structure. The observed values in the patterns closely matched those documented in the standard card (JCPDS card of ZnO : 01-070-8070). The crystal size of zinc oxide particles was calculated to be 27.18 nanometers using the Scherer formula. Other parameters such as the measured angle at the peak (101) and the full width at half maximum (FWHM) were employed to compute the approximate stress and strain. Negative stress marks indicated the presence of compressive stress, typically caused by distortions and defects in the crystal.

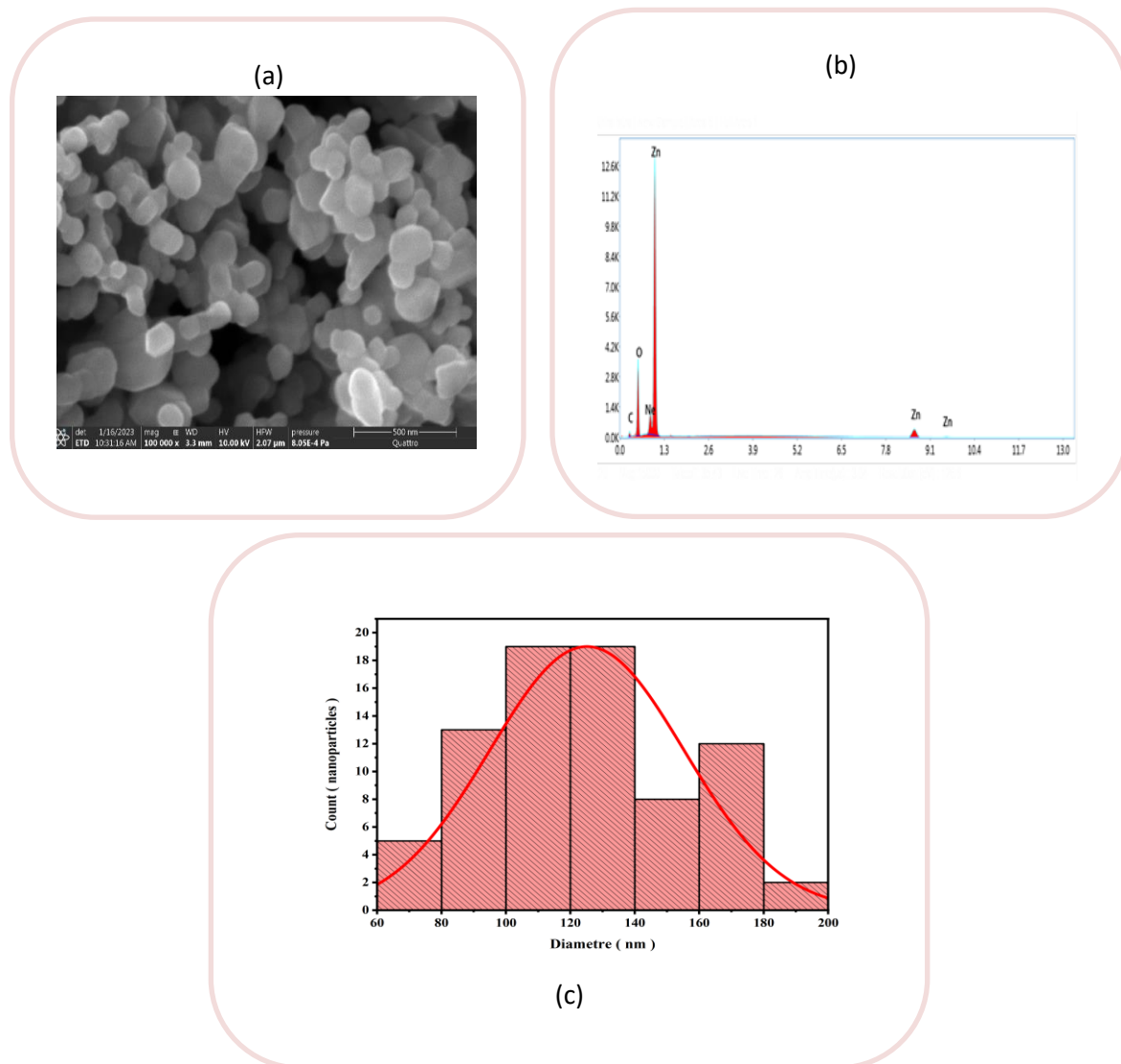


Cur-3. X-ray diffraction pattern of ZnO NPs

II.1.4 Scanning Electron Microscopy (SEM) + EDAX:

The scanning electron microscope (SEM) was utilized to examine the formation, size, shape, and morphology of the prepared sample's particles. The SEM images in Figure 6 at low magnification reveal a typical microstructure of zinc oxide particles, primarily consisting of various sizes and aggregated grains of nanoscale powder. Cur-4(a) illustrates the clustered arrangement of the particles, indicating their self-aggregation. Cur-4(b) illustrates the size distribution of zinc oxide particles, with the average particle size estimated at around 125 ± 60 nanometers. This size is significantly larger than the measurements obtained from XRD analysis. Additionally, SEM analysis can elucidate the general shape of the particles.

Energy-dispersive X-ray spectroscopy (EDAX) provides information about the chemical composition and atomic percentage of nanoparticles. Cur-4(c) shows the EDAX spectrum obtained for a sample of zinc oxide particles, revealing the presence of zinc, oxygen, and nitrogen. However, the carbon peak is not considered as it is absorbed by the surface region of zinc oxide particles.



Cur-4. SEM image of the ZnO NPs plasma synthesized with a magnification of (a) 100.00 KX; (b) their corresponding particle size distribution and (c) Atomic concentration and Typical EDAX spectra.

II.2 Photocatalytic activity:

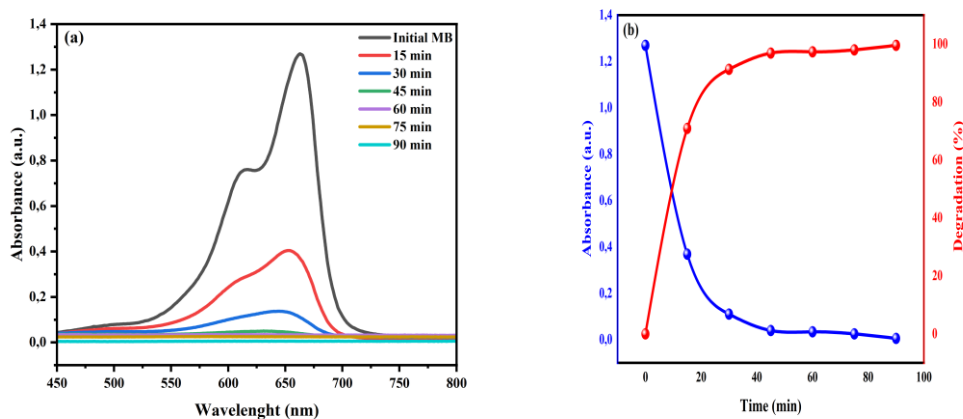
II.2.1 Under Sunlight:

illustrates the degradation of methylene blue dye in solution using photocatalysis with a catalyst under daylight (Cur-5). The figure contains two parts, (a) Absorption Spectrum of Dye Solution Over Time, This section shows how the dye's absorbance changes over time when exposed to daylight and the catalyst. Absorbance is measured at different intervals (initial, 15, 30, 45, 60, 75, and 90 minutes), At the maximum

wavelength (around 664 nm), absorbance initially is high, indicating a high dye concentration. Over time, it decreases significantly, indicating rapid degradation of dye molecules due to photocatalytic reactions under daylight.

(b) Change in Absorbance and Degradation Percentage Over Time, Shows a rapid decrease in absorbance, starting around 1.3 at 0 minutes and dropping to about 0.1 after 60 minutes, then stabilizing. Shows an increase in degradation percentage, starting from 0% at 0 minutes and reaching about 100% after 90 minutes, with most of the degradation occurring in the first 60 minutes.

The rapid decrease in absorbance over time indicates that daylight with the catalyst is very effective in degrading methylene blue dye. Most of the reaction happens in the first 30 minutes, with significant changes in absorbance and degradation percentage, and then the reaction slows down. Exposure to daylight with the catalyst generates reactive species like free radicals, which rapidly attack and degrade the dye molecules. This is evident from the quick reduction in absorbance and increase in degradation percentage. The results demonstrate the system's efficiency in degrading organic pollutants, such as dyes, using photocatalysis under daylight



Cur-5. (a) Absorbance spectra of dye solution under daylight irradiation, (b) photocatalytic degradation of dye at different times

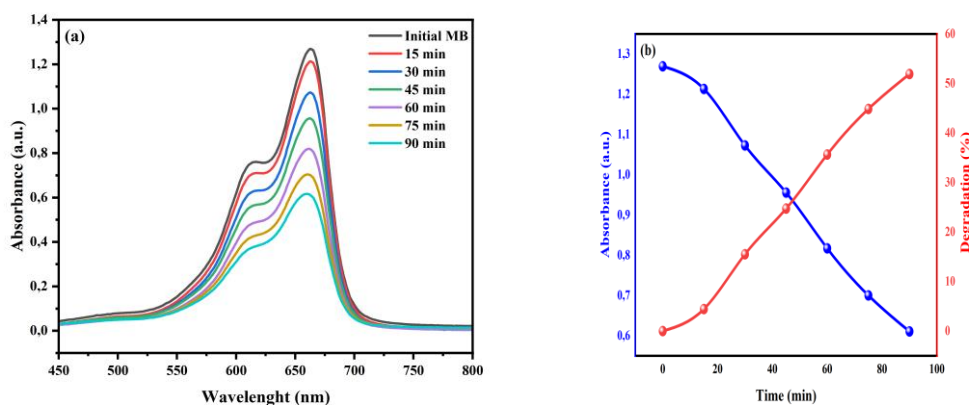
II.2.2 Under Plasma:

- Cur-6 illustrates the degradation of methylene blue dye in solution using photocatalysis with a catalyst under plasma influence. The figure has two parts, (a) Absorption Spectrum of Dye Solution Over Time, This part shows how the dye's absorbance changes over time when exposed to plasma and the catalyst. Absorbance is

measured at different intervals (initial, 15, 30, 45, 60, 75, and 90 minutes). The absorbance at the maximum wavelength (around 664 nm) gradually decreases, indicating the gradual degradation of dye molecules. Initially, the absorbance is high, reflecting a high dye concentration. Over time, it decreases, showing a reduction in dye concentration due to photocatalytic and plasma reactions.

(b) Change in Absorbance and Degradation Percentage Over Time, This part shows the relationship between the decrease in absorbance and the increase in degradation percentage over time. Absorbance starts at around 1.3 at 0 minutes and decreases to about 0.5 after 90 minutes, while the degradation percentage increases from 0% to about 50% over the same period. The inverse relationship between absorbance and degradation percentage confirms that the catalytic reactions effectively break down the dye molecules over time.

The significant decrease in absorbance over time indicates that plasma with the catalyst is effective in degrading methylene blue dye. Most of the reaction occurs in the first 60 minutes, with the absorbance and degradation percentage showing major changes, then the reaction slows down. Exposure to plasma and the catalyst generates reactive species, like free radicals, that attack and degrade the dye molecules. This is evident from the decrease in absorbance and increase in degradation percentage. The results demonstrate the efficiency of this system in degrading organic pollutants, such as dyes, through photocatalysis.

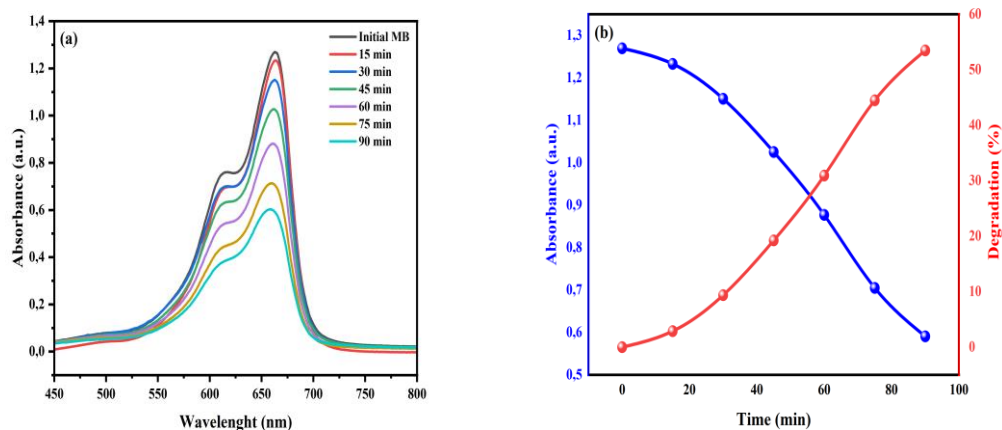


Cur-6. (a) Absorbance spectra of dye solution under plasma, (b) photocatalytic degradation of dye at different times.

- Cur-7 illustrates the degradation process of methylene blue dye in solution using photocatalysis with a catalyst under the influence of plasma. The Curve contains two parts, (a) Absorption Spectrum of Dye Solution Over Time This section shows how the absorbance of the dye's optical spectrum changes over time when exposed to plasma and the catalyst. Absorbance is measured at different time intervals (initial, 15, 30, 45, 60, 75, and 90 minutes). At the maximum wavelength (around 664 nm), the absorbance is initially high, reflecting a high concentration of the dye. Over time, the absorbance gradually decreases, indicating the gradual degradation of the dye molecules. This continuous decrease in absorbance indicates that the photocatalytic and plasma reactions are effective in degrading the dye over time.

(b) Change in Absorbance and Degradation Percentage Over Time, This section shows the relationship between the decrease in absorbance and the increase in the percentage of degradation over time. Absorbance and the degradation percentage are tracked from 0% to about 50% over 90 minutes. It is observed that absorbance decreases significantly over time, reflecting the reduction in dye concentration in the solution. At the same time, the degradation percentage gradually increases, being significant in the first 60 minutes and continuing to increase slowly thereafter. This inverse relationship between absorbance and degradation percentage confirms the effectiveness of the catalytic reactions in degrading the dye molecules.

The noticeable decrease in absorbance over time confirms that plasma with the catalyst is effective in breaking down the methylene blue dye molecules. The change in absorbance and degradation percentage shows that dye molecules are significantly degraded during the first 60 minutes of exposure, then the reaction continues slowly thereafter. Exposing the dye to plasma with the catalyst leads to the formation of reactive species, such as free radicals, which attack and break down the dye molecules. This degradation is clearly shown by the reduction in absorbance and increase in degradation percentage over time. The results indicate the efficiency of the system used in degrading organic pollutants, such as dyes, through photocatalysis. This method can be effectively used in treating water contaminated with dyes and other organic pollutants. This study highlights the importance and effectiveness of using plasma with catalysts in industrial wastewater treatment, providing an efficient method for reducing pollutant concentrations and improving water quality.



Cur-7. (a) Absorbance spectra of dye solution under plasma with catalyze (b) photocatalytic degradation of dye at different times

- Illustrate the degradation of methylene blue dye using photocatalysis under different conditions. Cur-5 shows degradation under daylight with a catalyst, where rapid degradation occurs, achieving near-complete degradation within 90 minutes. In contrast, Curve 6 and 7 show degradation under plasma influence with a catalyst, where the degradation is slower and more gradual, reaching about 50% after 90 minutes. Thus All methods are effective in the degradation of methylene blue dye, but daylight with a catalyst is the fastest and most efficient, while plasma-based methods provide stable and continuous degradation.

Conclusion

The integration of plasma technology with nanoparticles demonstrates significant potential in industrial wastewater treatment, leveraging the unique properties of both plasma and nanotechnology to effectively improve water quality and reduce pollution. Plasma generates active particles and ions that aid in breaking down chemical contaminants, while nanoparticles increase the interaction surface area and enhance the chemical response, leading to improved pollutant removal efficiency.

Our study has shown the great efficacy of combining plasma with zinc oxide nanoparticles, synthesized using the sliding arc discharge system, in degrading methylene blue dye, highlighting the broad application potential of this technology in industrial wastewater treatment. This method is characterized by its simplicity, speed, and sustainability, using air as a gas source.

With substantial improvements in water quality, this technology can reduce negative environmental impacts and preserve biodiversity in water bodies affected by industrial discharge, in addition to providing cost and resource savings in the treatment process. It also opens new opportunities for reusing treated water in other industries or in agricultural irrigation, thereby reducing the pressure on clean water sources.

The integration of plasma and nanotechnology offers an innovative and environmentally friendly solution for achieving clean and healthy water, contributing to the overall health of humans and the environment, and paving the way for further research and future applications in water purification.

Abstract:

In this study, we developed an efficient technique for synthesizing zinc oxide nanoparticles using a sliding arc discharge system, with the goal of integrating plasma and ZnO nanotechnology for water purification. The method is characterized by its simplicity, speed, and the use of air as a gas source, making it a sustainable option. Analyses showed that the produced nanoparticles, with an average size of 27 nanometers and an energy gap of 3.26 electron volts, are effective in degrading methylene blue dye. Photocatalysis under daylight was the fastest, while plasma-based methods provided stable degradation. We conclude that this technique holds promising potential for industrial wastewater treatment, opening new avenues for the application of plasma technologies in water purification.

The keywords : ZnO, nanoparticles, no-thermal plasma, traitement, wastewater.

Résumé :

Dans cette étude, nous avons développé une technique efficace pour la synthèse de nanoparticules d'oxyde de zinc en utilisant un système de décharge à arc glissant, dans le but d'intégrer les technologies du plasma et des nanoparticules de ZnO pour la purification de l'eau. La méthode se caractérise par sa simplicité, sa rapidité et l'utilisation de l'air comme source de gaz, ce qui en fait une option durable. Les analyses ont montré que les nanoparticules produites, avec une taille moyenne de 27 nanomètres et une bande interdite de 3,26 électrons volts, sont efficaces pour dégrader le colorant bleu de méthylène. La photocatalyse sous la lumière du jour était la plus rapide, tandis que les méthodes basées sur le plasma ont fourni une dégradation stable. Nous concluons que cette technique offre un potentiel prometteur pour le traitement des eaux usées industrielles, ouvrant de nouvelles perspectives pour l'application des technologies du plasma dans la purification de l'eau.

Mots-clés : ZnO, nanoparticules, plasma non thermique, traitement, eaux usées.

المخلص:

في هذه الدراسة، طورنا تقنية فعالة لتخليق جسيمات أكسيد الزنك النانوية باستخدام نظام تفريغ القوس المنزلق، بهدف دمج تقنيتي البلازما والنانو ZnO لتنقية المياه. تتميز الطريقة ببساطتها وسرعتها واستخدام الهواء كمصدر للغاز، مما يجعلها خياراً مستداماً. أظهرت التحليلات أن الجسيمات النانوية المنتجة بمتوسط حجم 27 نانومتر وفجوة طاقة 3.26 إلكترون فولت فعالة في تدهور صبغة الميثيلين الزرقاء، حيث كان التحفيز الضوئي تحت ضوء النهار الأسرع، بينما قدمت الطرق المعتمدة على البلازما تدهوراً مستقراً. نستنتج أن هذه التقنية تمتلك إمكانيات واعدة في معالجة مياه الصرف الصناعي، مما يفتح آفاقاً جديدة لاستخدام تقنيات البلازما في تنقية المياه.

الكلمات المفتاحية: ZnO، جسيمات نانوية، بلازما غير حرارية، معالجة، مياه الصرف

