PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

UNIVERSITY OF ECHAHID HAMMA LAKHDAR - EL OUED

FACULTY OF EXACT SCIENCES

DEPARTMENT OF CHEMSTRY

Dissertation Submitted in Partial Fulfillment of the Requirements for Master's Degree in:

Field: Chemistry

Specialty: Organic Chemistry

THEME

Using Medicinal Plant Extract for the Green Synthesis of Magnetic Nanoparticles Intended for Polluted Water Remediation: Optimization and Insights

Discussed on June 12th, 2024

Presented By:

- **Berrouba Kaouthar**
- **Homci Manar**
- **Hemissi Safa**
- **Degla Dikra manal**

Before the discussion Committee:

Pr. Ammar Zobeidi	**President**	**University of El Oued**
Dr. Ahmed Mehellou	**Examiner**	**University of El Oued**
Mr. Hamza Serraye	**Economic partner representative**	**ADE – El Oued**
Dr. Larbi Haddad	**Supervisor**	**University of El Oued**

Academic year: 2023/2024

PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

UNIVERSITY OF ECHAHID HAMMA LAKHDAR - EL OUED

FACULTY OF EXACT SCIENCES

DEPARTMENT OF CHEMSTRY

Dissertation Submitted in Partial Fulfillment of the Requirements for Master's Degree in:

Field: Chemistry

Specialty: Organic Chemistry

THEME

Using Medicinal Plant Extract for the Green Synthesis of Magnetic Nanoparticles Intended for Polluted Water Remediation: Optimization and Insights

Discussed on June 12th, 2024

Presented By:

- **Berrouba Kaouthar**
- **Homci Manar**
- **Hemissi Safa**
- **Degla Dikra manal**

Before the discussion Committee:

Pr. Ammar Zobeidi	**President**	**University of El Oued**
Dr. Ahmed Mehellou	**Examiner**	**University of El Oued**
Mr. Hamza Serraye	**Economic partner representative**	**ADE – El Oued**
Dr. Larbi Haddad	**Supervisor**	**University of El Oued**

Academic year: 2023/2024

شكر وتقدير

إلى من علمونا أبجدية الحياة إلى من أضاؤوا لنا قناديل العلم والمعرفة والعطاء شكرا لكل من علمنا حرفا طيلة مسيرتنا الدراسية لكم كل الشكر والتقدير والإحترام ...

إلى كل من ساعدنا للمضي قدما في هذا الطريق المشحون بالعلم والمعرفة ...

إلى كل من شاركنا علمه وخبراته بكل أمانة وصدر رحب ...

شكر وتقدير خاص إلى أستاذنا المتألق دائما الدكتور **العربي حدّاد** ، نشكره على تأدية الأمانة بكل صدق و على معلوماته الثمينة وأفكاره المتميزة دائما وإنضباطه وتفانيه في العمل ... نسأل الله أن يديم عليه الصحة والعافية ويمده بالعمر الطويل و العلم العظيم الوافر

كما نتقدم بأخلص عبارات الشكر للجنة الموقرة : البروفيسور عمار زبيدي رئيسا ، الدكتور أحمد محلو مناقشا ، و السيد الفاضل حمزة سراي ممثلا عن الشريك الاقتصادي لقبولهم مناقشة مذكرتنا و إثرائها

كما لا يفوتنا أن نتقدم بشكرنا لكل مهندسي المخابر البيداغوجية لقسم الكيمياء و مخابر كلية علوم الطبيعة و الحياة على تسهيل مهامنا خلال فترة بحثنا

و أخيرا و ليس آخرا ، نشكل كل من قدم لنا يد العون من قريب أو من بعيد

الإهداء

الحمد الله الذي رزقنا وسخر لنا هذا رحمة منه والحمد الله الذي رزقني لمن اهدي

كلماتي هذه

لمن كان سبب في وجود أمي وأبي حفظهما الرحمان

إلى سندي وعضدي إخوتي

لي كل افرد عائلتي

شكرا لكم على كل لحظة كنتم فيها عونا وسندا لي

. ولكل من ساهم في انجاز هذه المذكرة

منار

الإهداء

بعد مسيرة دراسية دامة سنوات حملت في طياتها الكثير من الصعوبات والمشقة والتعب، ها أنا اليوم أقف على عتبة تخرجي اقطف ثمار تعبي وارفع قبعتي. بكل فخر، فاللهم لك الحمد قبل ان ترضى ولك الحمد إذا رضيت ولك الحمد بعد الرضا، لأنك وفقتني على إتمام هذا العمل وتحقيق حلمي .... اهدي هذا العمل

الى المرآة التي صنعت مني فتاة طموحة وتعشق التحديات، قدوتي الأولى التي منها تعرفت على القوة والثقة بالنفس لمن رضاها يخلق لي التوفيق (أمي) أطال الله في عمرك بالصحة والعافية.

إلى ذلك الرجل العظيم الذي أخرج أجمل ما في داخلي وشجعني دائماً للوصول إلى طموحاتي، رَجُلٍ عَلمني الحياة بأجمل شكل وبذل كل ما بوسعه ولم يبخل (أبي) أدامك الله ظلاً لنا.

إلى ضلعي الثابت وأماني إلى ما شددت عضدي بهم فكانوا لي ينابيع ارتوي منها إخوتي)خالد، أكرم، الأمين(

إلى شريكة ورفيقة الخندق التي تقاوم الحياة بالضحك، ملاكي الحارس التي كانت دوماً موضع الإكاء في عثراتِ حياتي صديقتي وتوأم روحي (إيمان) أستودعك الله الذي لا تضيع ودائعه.

إلى جميع من أمدوني بالقوة والتوجيه وآمن بي ودَعَمَني في الأوقات الصعبة لأصل إلى ما أنا عليه الآن دمتم لي سندا لا عمر له .....

كوثـــر

الإهداء

الحمد لله الذي تتم بنعمته الصالحات اللهم لك الحمد ولك الشكر كما ينبغي لجلال وجهك وعظيم سلطانك اللهم لك الحمد كله وإليك يرجع الأمر كله

أهدي هذا العمل لنفسي أولا .....

إلى روح أمي فقيدتي رحمها الله لعل هذا العمل صدقة جارية لروحها الطاهرة

إلى أبي سندي وضلعي الثابت حفظه الله ورعاه

إلى أمي الثانية على دعمها الدائم لي رعاها الله

إلى أخي الوحيد على لطفه وحبه ومساندته لي سدد الله خطاه وأمتعه الصحة والزرق والأمان

إلى أخواتي على إيمانهم بي ودعمهم النفسي لي رعاهم الله وحفظ أولادهم واجعلهم في المراتب العليا

إلى أحبتي وكافة أصدقائي .....

إلى Clinic-Benseghir على دعمهم لي في كافة الأوقات

أتمنى أن أكون مصدر فخر لكم جميعا ...

صفـاء

الإهداء

بسم الله الرحمن الرحيم والصلاة والسلام على اشرف الأنبياء والمرسلين نبينا وشفيعنا صلى الله عليه وسلم، أما بعد :

ها هي الأيام قد مرت بسرعة حتى نصل إلى نهاية مشوارنا الدراسي وها نحن اليوم والحمد لله نطوي سهر الليالي وتعب السنين ...

إلى منارة العلم ..إلى سيد الخلق أمام المرسلين ..الامي الذي علم المتعلمين

* سيدنا محمد صلى الله عليه وسلم *

إلى من لا يضاهيهما أحدا في الكون إلى من أمرنا الله ببرهما ،إلى من بذلا الكثير ،وقدما ما لا يمكن أن يرد إليكما تلك الكلمات : أمي وأبي أطال الله في عمرهما

اهدي لكم هذا البحث فقد كنتما خير داعم لي طوال مسيرتي الدراسية.

إلى من كانوا سندا لي على حمل الحياة ومصاعبها تشجيعا لي حتى وصلت إلى هنا أخوتي مصدر إلهامي:

محمد ادم سيف الدين *الياس *يحي * قتيبة *همام* والكتكوتة أسيل المنتهئ *

إلى روافد الوفاء إلى نبع المحبة والحنان وأغلى ما املك صديقاتي أخواتي العزيزات:

مسعودة *صفاء *خديجة*سمية *دعاء * سندس *

كما اهدي تخرجي إلى الأساتذة الأفاضل و على رأسهم الأستاذ حداد العربي الذي لم يبخل علينا حتى حصولنا على هذا المنال.

إلى كل من ساندني من قريب أو بعيد لكم مني جزيل الشكر.

منال ذكرى

Abstract

Green synthesis of iron oxide nanoparticles using natural plant extracts is a promising alternative to traditional synthesis methods. It is considered a sustainable and environmentally friendly solution.

In this work, iron oxide nanoparticles were synthesized using a Mentha spicata plant extract and a 0.04 M iron chloride solution ($FeCl_3$). The successful green synthesis of iron oxide particles was confirmed using both ultraviolet (UV) and band gap (Eg)spectroscopy, infrared (FTIR) analysis, scanning electron microscopy (ESM), X-ray diffraction (XRD). The pH was also measured at Zero point (pzcpH). Ultraviolet (UV) analysis shows maximum absorption at 303nm, and FTIR shows an absorption band at 400-500 indicating the vibration of the Fe–O bond. The value of pzcpH was about 7.4. The factors affecting the adsorption yield were also studied, which are a mass index. The adsorbent material (25-100), the pH of the medium (4-10) and the contact time (30-120). To determine the optimal conditions for adsorption using surface response modeling, a yield of 86.5% was reached. The ability of iron oxide nanoparticles to inhibit DPPH free radicals was also demonstrated.

Keywords :Green synthesis, Iron oxide nanoparticles, mentha spicata, adsorption

Résumé

La synthèse verte de nanoparticules d'oxyde de fer à partir d'extraits naturels de plantes est une alternative prometteuse aux méthodes de synthèse traditionnelles. Elle est considérée comme une solution durable et respectueuse de l'environnement.

Dans ce travail, des nanoparticules d'oxyde de fer ont été synthétisées à l'aide d'un extrait de plante Mentha spicata et d'une solution de chlorure de fer 0,04 M ($FeCl_3$). La synthèse verte réussie de particules d'oxyde de fer a été confirmée par spectroscopie ultraviolette (UV) et à bande interdite (Eg), analyse infrarouge (FTIR), microscopie électronique à balayage (ESM) et diffraction des rayons X (XRD). Le pH a également été mesuré au point zéro (pzcpH). L'analyse ultraviolette (UV) montre une absorption maximale à 303nm, et le FTIR montre une bande d'absorption à 400-500 indiquant la vibration de la liaison Fe–O. La valeur de pzcpH était d'environ 7,4. Les facteurs affectant le rendement d'adsorption ont également été étudiés, qui sont un indice de masse. Le matériau adsorbant (25-100), le pH du milieu (4-10) et le temps de contact (30-120). Pour déterminer les conditions optimales d'adsorption à l'aide de la modélisation de la réponse de surface, un rendement de 86,5 % a été atteint. La capacité des nanoparticules d'oxyde de fer à inhiber les radicaux libres DPPH a également été démontrée.

Mots clés :Synthèse verte, Nanoparticules d'oxyde de fer, mentha spicata, adsorption

الملخص

التوليف الأخضر لجزيئات أكسيد الحديد النانوية باستخدام المستخلصات النباتية الطبيعية •هو بديل واعد للطرق التوليف التقليدية .حيث يعتبر حلا مستداما وصديقا للبيئة .

تم في هذا العمل اصطناع جسيمات أكسيد الحديد النانوية باستخدام مستخلص نبات mentha spicata ومحلول كلوريد تم تأكيد التوليف الأخضر الناجح للجسيمات أكسيد الحديد باستعمال كل من طيف الأشعة . M0.04 ذو تركيز $FeCl_3$ الحديد فوق البنفسجية(UV) وفجوة النطاق (Eg) ،تحليل الأشعة تحت الحمراء(FTIR) ،مجهر المسح الالكتروني(MSE) ، الحيود السينية (XRD) كما تم قياس درجة الحموضة عند نقطة الصفر(pzcpH).يظهر تحليل الأشعة فوق بنفسجية(UV) أقصى امتصاص عند303 نانومتر وتظهر الأشعة (FTIR) عصابة امتصاص عند500-400 تدل على اهتزاز الرابطة Fe-O كما بلغت قيمة pzcpH حوالي 7.4.تمت أيضا دراسة العوامل المؤثرة على مردود الامتزاز وهي كتالي كتلة المادة المازة (100-25)،درجة حموضة الوسط (10-4) و زمن التلامس(120-30) لتحديد الشروط المثلى لامتزاز باستعمال نمذجة استجابة الأسطح ،تم توصل إلى مردود86.5 % . كما تم إظهار قدرة تثبيط الجسيمات أكسيد الحديد النانوية لجذور الحرة DPPH.

الكلمات المفتاحية: الاصطناع الأخضر،جسيمات أكسيد الحديد النانونية؛ mentha spicata ،الإمتزاز.

LIST OF ABBREVIATIONS

Abbreviation	Meaning
Fe_2O_3	Iron (III) oxide
$FeCl_3$	Iron chloride
Eg	band gap
NPs	Nanoparticles
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
ANOVA	Analysis of variance
MB	Methylene blue
CV	Crystal violet
CR	Congo red
MO	Methyl orange
PFO	Pseudo-first-order
PSO	Pseudo-second-order
DPPH	2.2- diphényl-1-picrylhydrazy
RC_{50}	The concentration of the extract that inhibits half the amount of DPPH radical formed

LIST OF SYMBOLS

Code	Meaning
Fe^{+2}	Ferrous ions
Fe^{+3}	Ferrous ions
$\propto Fe_2O_3$	Hematite

Fe_2O_3	Magnetite
γFe_2O_3	mMghemite
UV	Ultraviolet light
λ_{max}	Maximum wavelength
A	Adsorbance
pHz	pH at point zero charge
m	mass
T	Temperature
t	time
V	Volume
C	Concentration
C_0	Initial concentration of an adsorbent
C_e	Concentration of the adsorbent at equilibrium
K_1	Quasi-first order adsorption velocity constant
K_2	Quasi-second order adsorption velocity constant
K_{dif}	The diffusion rate constant within the particles
q_e	Quantity adsorbed at equilibrium
q_t	Quantity adsorbed over time
q_{max}	Maximum adsorbed quantity
R	Rejected
R^2	Regression coefficient
α	The absorption parameter
$h\nu$	The photon energy

Liste of Figures

Liste of Tables

Table of contents

Introduction

Background and Context

Water pollution remains one of the most significant global challenges, affecting ecosystems, human health, and economic activities. The escalating levels of industrialization, urbanization, and agricultural practices have contributed to the contamination of water bodies with a variety of pollutants, including heavy metals, organic compounds, and pathogens. Traditional water treatment methods, while effective to some extent, often fall short in dealing with the complexity and persistence of modern contaminants. This has led to an increasing demand for innovative materials and technologies capable of providing efficient and sustainable water purification solutions **[1]**.

Nanotechnology has emerged as a promising field, offering unique opportunities for water treatment applications. Nanoparticles (NPs) are of particular interest due to their high surface area, enhanced reactivity, and tunable physical and chemical properties. Among the various types of NPs, magnetic iron nanoparticles (MNPs) stand out due to their ease of separation from water using an external magnetic field, which enhances the practicality and efficiency of the treatment process **[2]**.

Research Problem or Gap

Despite the advantages of nanoparticles, conventional synthesis methods often involve hazardous chemicals and energy-intensive processes, posing environmental and health risks. The development of green synthesis methods, which utilize natural plant extracts for the production of nanoparticles, presents a sustainable and environmentally friendly alternative. However, the application of green-synthesized magnetic iron nanoparticles in water treatment is still in its nascent stages, with limited research addressing their synthesis, characterization, and practical efficacy **[3, 4]**.

This research seeks to bridge this gap by exploring the use of Mentha spicata (spearmint) extract in the green synthesis of magnetic iron nanoparticles. Mentha spicata, known for its rich content of bioactive compounds, offers a dual function as both a reducing and stabilizing agent in the nanoparticle synthesis process. The resulting nanoparticles are expected to exhibit enhanced properties suitable for water treatment applications **[5, 6]**.

Research Questions or Objectives

The primary objective of this study is to develop a sustainable and efficient method for synthesizing magnetic iron nanoparticles using Mentha spicata extract and to evaluate their performance in water treatment. The specific research questions addressed in this thesis are:
How can Mentha spicata extract be utilized in the green synthesis of iron nanoparticles?

How effective are the synthesized magnetic iron nanoparticles in removing water contaminants through adsorption and photocatalysis?

Significance of the Study

The significance of this study lies in its contribution to the development of sustainable water treatment technologies. By utilizing Mentha spicata for the green synthesis of magnetic iron nanoparticles, this research aligns with the principles of green chemistry, reducing the reliance on toxic chemicals and minimizing environmental impact. The synthesized nanoparticles, characterized by advanced analytical techniques, are expected to demonstrate high efficiency in contaminant removal, thus offering a viable solution to water pollution **[7]**. Moreover, this study provides a comprehensive understanding of the synthesis process, the properties of the nanoparticles, and their practical application in water treatment. The insights gained from this research can inform future studies and industrial applications, fostering the development of eco-friendly nanomaterials for environmental remediation **[8]**.

Overview of the Thesis Structure

This manuscript is structured to provide a thorough exploration of the research undertaken, comprising the following chapters:

Chapter 1: In this chapter, we will provide an overview of nanotechnology and its various applications. We will focus in particular on iron oxide nanoparticles and their unique properties

Chapter 2: This chapter discusses the features of the studied plant, and some important aspects related to this plant.

Chapter 3: This chapter provides a comprehensive analysis of the adsorption phenomenon, including its mechanisms and factors affecting it, in addition to a review of the most prominent isotherm models used in the field of treating polluted water and their role in designing and improving pollutant removal processes.

Chapter 4: This chapter describes the materials and methods used to synthesize magnetic iron nanoparticles using ethanolic mint extract. This chapter also details the characterization techniques (XRD, FTIR, SEM, and EDX) used to analyze nanoparticles, and details the photocatalytic process for water treatment as well as the experimental setup for water treatment applications, focusing on adsorption and photo catalysis.

Chapter 5: This chapter presents the results obtained from the synthesis and characterization of nanoparticles, and discusses their structural, morphological and compositional properties. It also evaluates the performance of nanoparticles in water treatment, analyzing their effectiveness in removing pollutants and the basic mechanisms involved.

References

.1 Singh, P., et al., *Biological synthesis of nanoparticles from plants and microorganisms.* Trends in biotechnology, 2016. **34**(7): p. 588-599.

.2 Sharma, V.K., et al., *Natural inorganic nanoparticles–formation, fate, and toxicity in the environment.* Chemical Society Reviews, 2015. **44**(23): p. 8410-8423.

.3 Iravani, S., *Green synthesis of metal nanoparticles using plants.* Green chemistry, 2011. **13**(10): p. 2638-2650.

.4 Ahmad, T., et al., *Biosynthesis, structural characterization and antimicrobial activity of gold and silver nanoparticles.* Colloids and Surfaces B: Biointerfaces, 2013. **107**: p. 227-234.

.5 Wang, S. and H. Wu, *Environmental-benign utilisation of fly ash as low-cost adsorbents.* Journal of hazardous materials, 2006. **136**(3): p. 482-501.

.6 Gupta, V.K., et al., *Photo-catalytic degradation of toxic dye amaranth on TiO2/UV in aqueous suspensions.* Materials science and engineering: C, 2012. **32**(1): p. 12-17.

.7 Barhoum, A., et al., *Review on natural, incidental, bioinspired, and engineered nanomaterials* : *history, definitions, classifications, synthesis, properties, market, toxicities, risks, and regulations.* Nanomaterials, 2022. **12**(2): p. 177.

.8 Khandel, P., et al., *Biogenesis of metal nanoparticles and their pharmacological applications: present status and application prospects.* Journal of Nanostructure in Chemistry, 2018. **8**: p. 217-254.

CHAPTER I

Theoretical study of nanotechnology and iron oxide

I. Introduction

Following a wave of scientific revolutions in physics, chemistry, biology, and engineering, nanotechnology has emerged as one of the most significant and cutting-edge technologies because of its influence on a number of life because it permeates everything around us.In material science, one of the most promising advances is nanoscience and nanotechnology.The definition of the word nano is tiny technology or technologytiny pieces .Another way to define nanotechnology is as a branch of research and invention that focuses on creating objects (materials and technologies) on the scale of atoms and molecules.

I.1. What is meant by nano?

Nano, like micro, pico, and so on, is a prefix used in front of a macroscopic unit to change its value by orders of magnitude. Nano means one billionth, or 10^{-9}. Thus, one nanometer is one billionth of a meter. When placed in front of words like science and technology, however, the meaning of nano is not that obvious (nanoscience cannot be one billionth of science!). Since experimental science and technology deal with material objects, it seems fair to say that nanoscience and nanotechnology are science and technology concerning objects of nanometer dimensions, which are atoms (on a scale of tenths of nanometers) and molecules (on a scale of nanometers). In theory, nanoscience and nanotechnology may be considered to encompass all fields of science and technology, as everything is composed atoms and molecules. Limiting these terms to the fields of study and technology that are especially concerned with the atomic and molecular makeup of macroscopic matter is an additional option. However, neither physicists nor chemists would concur on defining nanoscience and nanotechnology in this way, therefore both options are inadequate. Focusing on the inherent characteristics of nanoscale items and the potential for using, modifying, or assembling them into assemblies to carry out certain tasks can lead to a more accurate description of nanoscience and nanotechnology. These ideas make more sense when considered in the context of a miniaturization discussion **[1]**.

I.2. Definition of nanoscience

The study of phenomena, their analysis, and material manipulation at the nanoscale—that is, between one and 100 nanometers is known as nanoscience. Thanks to tiny size effects and particular surface interactions, materials at this scale display unique physical, chemical, and biological features that set them apart from those at larger scales. The goal of nanoscience is to comprehend these phenomena and use them to create novel applications in a variety of domains, including energy by increasing the efficiency of solar cells and batteries, electronics by creating smaller and faster components, and medicine by creating drugs and nanoparticles

to improve treatment. To accomplish sustainable technological and scientific progress, nanoscience blends physics, chemistry, biology, and engineering in a multidisciplinary manner **[2]**.

I.3. Nano technique

Nanotechnology is a reliable and environmentally friendly process of synthesizing nanoparticles **[3]**, and "nanotechnology" is a generic term that describes applications in many scientific fields but generally covers research into the principles and properties that exist at the nanometer scale **[4]**. Although nanotechnology is a new word, it is not an entirely new field. Nature has created many objects and processes that operate on the micro to nano scale. The new behavior of nanoparticles at the nanoscale is not necessarily predictable from that observed at large scales. Important changes in behavior are not only caused by order of magnitude reduction but also by new phenomena such as size limitation, the prevalence of interfacial phenomena, quantum mechanics, and Coulomb blocking **[5]**.

I.4. Principles of Nano technique excellence

Fundamental concepts that set nanotechnology apart and allow it to fundamentally alter a wide range of applications are what make it possible. These are a few of the fundamental ideas that set nanotechnology apart:

I.4.1. Atomic-Level Control

By providing exact control over materials and structures at the atomic level, nanotechnology opens up new possibilities for creating materials with particular characteristics.

I.4.2. Change in Property

Materials at the nanoscale have completely different properties from those of their macroscopic counterparts, which opens up new and cutting-edge applications.

I.5. Diverse Applications

The relevance of nanotechnology in the growth of science and It is not an exaggeration to say that nanotechnology can be a threat to many industries due to the fact that it often offers smaller, cheaper, and faster devices with superior functionality while using less raw materials and energy**[8, 9]**. It has the potential to affect the production of virtually every synthetic object, from automobiles, electronics, advanced diagnostics, and surgery, to advanced medicines and tissue/bone substitutes. Today’s nanotechnology takes advantage of current advances in chemistry, physics, materials science, biotechnology, and electronics to create new materials that have unique properties. Some of the applications of nanotechnology have already made their mark on the market, while others are being intensively researched for

solutions to humanity's biggest problems: diseases, clean energy, clean water, etc. The products of advanced nanotechnology that will be available in the coming decades promise even more revolutionary applications than the products of current and near-future nanotechnology **[10]**. Nevertheless, the remainder of this literature review describes in very general terms selected areas of application of nanotechnology products. In addition, Figure 1 collects the applications most frequently mentioned in the literature without distinguishing between those already on the market and those in the research phase **[11]**.

I.5.1. Energy and Environment

The uncertain future of traditional energy sources and increasingly new environmental policies have contributed to a global movement to develop and implement alternative methods of energy extraction and efficient energy use. Nowadays, Nano technological inventions are penetrating into various subsystems of the entire energy system, starting from energy acquisition, conversion, distribution, and storage and ending with energy utilization**[12, 13]**. The application of nanotechnology in the energy field, which includes lithium-ion batteries, fuel cells, light emitting diodes, ultra-capacitors, and solar cells, among others, is a hot topic in many scientific studies. Unfortunately, the development of this field of nanotechnology has been hampered by significant production costs compared to that of conventional technologies**[14]**. Today, thanks to nanomaterials, photovoltaic cells are increasing their efficiency while reducing the cost of electricity production at an unprecedented rate. The production, storage, and conversion of hydrogen into electricity in fuel cells benefit from more efficient water-splitting catalysts, better-nanostructured materials for higher hydrogen adsorption capacity, and cheaper yet simpler fuel cells**[12]**.

I.5.2. Electronics

Miniaturization of electronic devices is considered a key factor in achieving higher efficiency and speed of information exchange. This achievement is now available mainly due to great advances in nanolithography techniques. Thanks to the nanotechnology-based approach, the performance of traditional semiconductors has increased, and new possibilities have emerged **[12]**. Creating more efficient computer processors is another advantage of Nano electronics, which can improve the capabilities of electronic components in several ways: (i) by improving the screens displayed on electronic devices, which includes reducing power consumption while reducing the weight and thickness of the screens, (ii) by increasing the density of memory chips, and (iii) by reducing the size of transistors used in integrated circuits **[15]** Products of nanotechnology are also used in supercapacitors which are a type of electrochemical capacitors and have been recognized as some of the most reliable and

efficient energy storage and conversion devices. For example, nanowires are being produced and used as electrode material for supercapacitors **[16, 17]**.

I.5.3. Agro-Food Production

Well as in all areas of the food industry, which include improved food quality and safety, reduced agricultural inputs, enriched nutrient absorption from the soil, pathogen detection, food processing, and packaging, delivery of bioactive compounds to destinations, and production of nanotechnology-based food additives. New approaches based on nanotechnology lead to increased safety and nutritional value of food products, reduced chemical spreading, minimized nutrient losses in fertilization, and increased yields through pest control**[18]**. In addition, new agrochemicals and new delivery mechanisms have been developed based on Nano technological devices to improve crop yields and reduce pesticide use**[19]**.

I.5.4. Cosmetics

Applications of nanotechnology and nanomaterials can be found in many cosmetic products, including moisturizers, hair care products, makeup products, and sunscreens**[20, 21]**. Novel Nano carriers with various formulations, such as liposomes, noisome, Nano emulsions, micro emulsions, solid lipid nanoparticles, nanostructured lipid carriers, and Nano spheres, have replaced the use of conventional delivery systems. These novel Nano carriers have the advantages of increased skin penetration (vitamins and other antioxidants), controlled and prolonged drug release, greater stability (unsaturated fatty acids, vitamins, antioxidants encapsulated in nanoparticles), site targeting, high entrapment efficiency, and improved aesthetics of the final product (e.g., in mineral sunscreens, making the particles of the active mineral smaller; they can be applied without leaving a noticeable white film)**[12, 19]**. However, it should be mentioned that Nano toxicological studies have shown concern about the impact of the increased use of nanoparticles in cosmetics, as there is the potential for them to penetrate the skin and cause health risks**[22, 23]**.

I.5.5. Medicine

Since several components of living cells are nanoscale in size, it was foreseeable that nanotechnology would be useful in biology and medicine. Today, some nanoscale materials have found clinical applications, and the field of nanomedicine has emerged as a result. As one of the main parts of nanotechnology, nanomedicine aims to provide more efficient tools for preventing and treating various diseases through the interaction of nanomaterials with biological molecules. Strategies based on nanomedicine have opened up new horizons for biomedical engineers as well as clinicians in the prevention, diagnosis, and treatment of

serious diseases. With nanotechnology applied to medicine, significant improvements have been witnessed in drug delivery systems, protein detection, cancer treatment, medical imaging and diagnostic platforms, implantable materials, and tissue regeneration strategies, among others **[24]**. It should be mentioned that various Nano systems have already been used for the benefit of human health, and a larger number of medical projects are underway.

I.5.6. Military and Security

Looking at nanotechnology in the light of national security, it is the latest means by which military weapons can be reduced in size and weight while maintaining the same performance or even increasing it. The potential use of nanotechnology in military applications encompasses almost every aspect, from civilian applications such as ultralight clothing and footwear for the individual warrior to advanced information-processing electronics that can be embedded in a variety of materials **[25]**. It is certain that nanotechnology will also be used in the military field to design new weapons with unique properties, such as small self-steering mini-robot missiles and the creation of devices that can collect water in all conditions. With all this, it is important to remember that Nano technological products have a powerful impact on the world, but if they are used for the wrong purposes, the damage could be irreversible, for dealing with nanotechnology is about testing our humanity, ethics, and knowledge **[26]**.

I.5.7. Water treatment

Nanotechnology's special qualities at the nanoscale allow it to provide creative and effective water treatment solutions. The utilization of adsorptive nanomaterials like graphene oxide and carbon nanotubes, which efficiently absorb chemical contaminants and heavy metals, as well as nanofiltration membranes, which offer high efficiency in eliminating fine particles and impurities, are notable uses. Furthermore, when exposed to light, nanoparticles such as titanium dioxide are utilized as photocatalysts, assisting in the breakdown of microorganisms and organic contaminants. Furthermore, antimicrobial nanoparticles are designed to kill bacteria and viruses efficiently, thus purifying water. Compared to more conventional approaches, these technologies help provide clean and safe water in more effective and efficient ways **[27]**.

I.6. Nanoparticles

I.6.1. Definition of nanoparticles

Nanoparticles are defined as the smallest unit that has chemical and physical properties for volumetric matter. It is a collection of a few hundred to a few thousand of atoms, forming a body with at least one dimension between 1 and 100 nanometers. A comparison with natural organic structures nanoparticles are in the size range compatible with protein **[28, 29].**

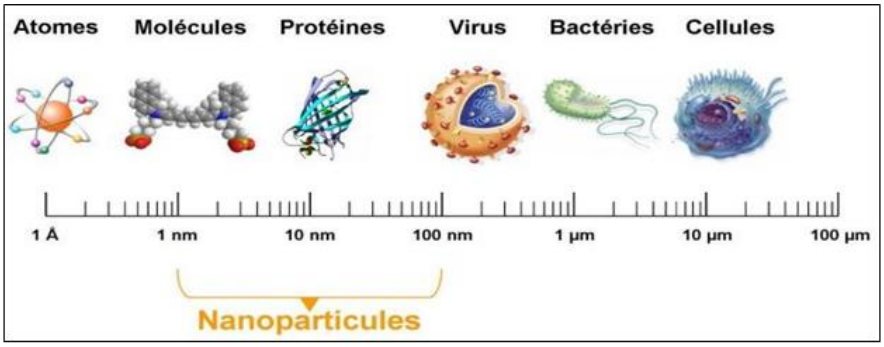


Figure I.1: A range of nanoparticle sizes compared to the sizes of major chemical and biological structures **[29]**.

I.6.2. Classification of nanoparticles

Understanding the properties of nanoparticles and their numerous applications requires first classifying them. Based on certain particle qualities, it also aids in behavior prediction, efficiency improvement, and the development of new technologies are typically divided into three categories: organic, inorganic and carbon materials **[30]**.

I.6.2.1. Organic nanoparticles

This class comprises NPs that are made of proteins, carbohydrates, lipids, polymers, or any other organic **[31]**. The most prominent examples of this category are dendrimers, liposomes, micelles, and protein complexes these nanoparticles (Ferritin) are usually non-toxic, biodegradable, and have two or more dimensions. Organic nanoparticles are sensitive to thermal and electromagnetic radiation such as heat and light. In addition, organic NPs are mostly used in the biomedical field in targeted drug delivery and cancer therapy **[32]**.

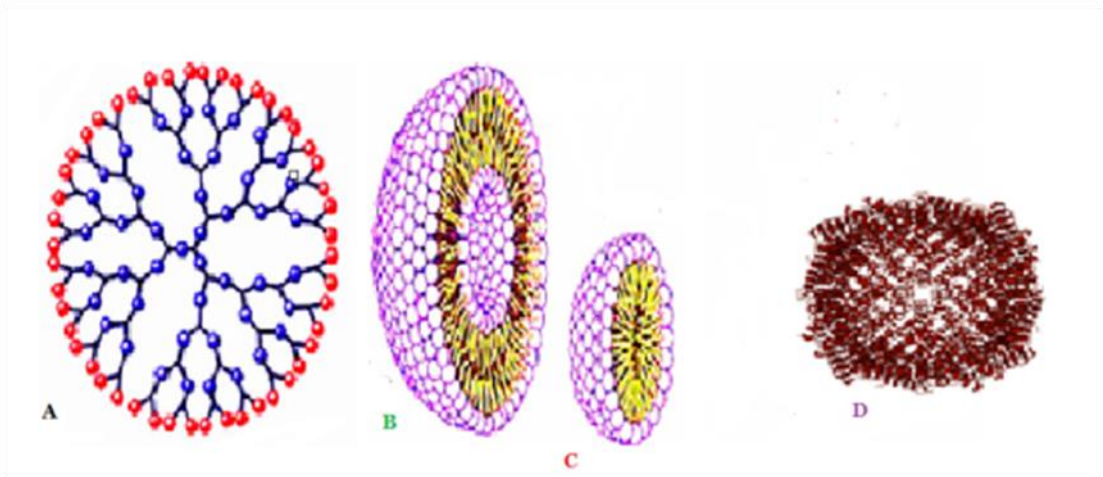


Figure I.2: Organic nanoparticles: a – Dendrimers, b – Liposomes , c – micelles and D– ferritin **[33]**.

I.6.2.2. Inorganic nanoparticles

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide based nanoparticles are generally categorised as inorganic nanoparticles **[33]**.

a. Metal-based

They are nanoparticles with a metal base which are manufactured from nanometer-sized metals, either destructively or constructively, it can be obtained from metals such as aluminum (Al), gold (Au), silver (Ag), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) **[33]**. Transition metals were found to be better for the synthesis of metal-based NPs due to the presence of partially filled d orbitals making them more redox active. These nanoparticles exhibit diverse shapes, including spherical and cylindrical forms. Leveraging their distinct characteristics, metal nanoparticles find widespread application across various domains such as sensors, photonics, environmental remediation, and medicine**[34]**.

b. Based on metal oxides

Nanoparticles are manufactured based on metal oxide to modify the properties of mineral-based nanoparticles, For example, iron nanoparticles (F_e) are quickly oxidized to iron oxide. Its reactivity rises when exposed to room temperature oxygen. in contrast to nanoparticles of iron. The primary reason for synthesizing metal oxide nanoparticles is their heightened reactivity and efficiency **[32]**.

c. Carbon based

Nanoparticles made entirely of carbon are known as carbon-based. Two main classes of carbon-based NPs are fullerenes and carbon nanotubes (CNTs). Other classes of carbon-based NPs are graphene, nanofibers, carbon black, and sometimes nano-sized activated carbon, and are shown in **Figure I.3** **[32].**

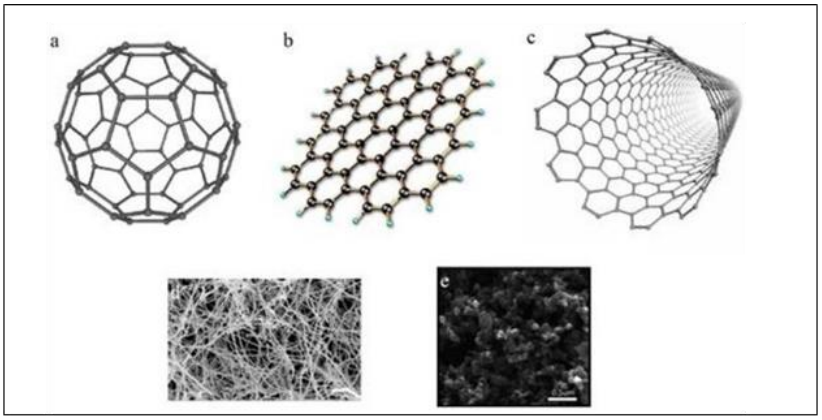


Figure I.3: Carbon based nanoparticles: a – fullerenes, b – graphene, c – carbon nanotubes, d – carbon nanofibers and e – carbon black.

I.6.3. Synthesis of Nanoparticles

Nanoparticles are manufactured in many different ways and methods with varying degrees of quality, speed and cost despite all these methods, they can be classified under two methods: bottom-up or top-down method. A simplified representation of the process is presented in **Figure I.4** **[31]**.

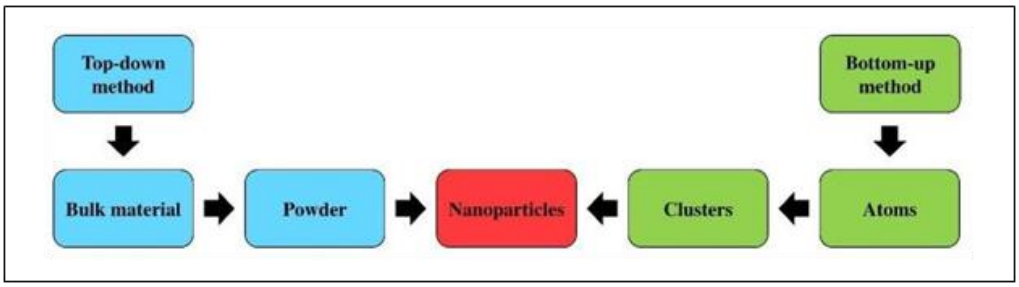


Figure I.4: Synthesis process.

- **Top-down method**

Top-down methods are the simplest and rely on breaking down bulk materials into nanoparticles. It is a destructive method, which are broken down into parts, or into nanometer particles when an energy source is applied this applied energy can be mechanical, chemical or thermal, or it can also be another form of energy such as laser radiation[35].

a. Mechanical milling method

It is most used to produce various nanoparticles where different elements are ground Inert atmosphere to reduce particle size. It is one of the least expensive ways to produce nanomaterials in large quantities **[36]**.

b. Nanolithography method

It involves printing the necessary structure or shape on a material that is sensitive to light, then carefully removing some of the material to get the desired structure and shape. Using a concentrated electron or light beam, lithography is a useful technique for building nanoarchitectures. Key advantages of nanolithography include the ability to produce nanoparticles of specific shapes and sizes in large quantities from a single nanoparticle. However, disadvantages include the need for sophisticated equipment and the associated costs**[33]**.

Laser ablation method

Nanoparticles from in-solution laser ablation synthesis is a common method a strong laser beam is used in laser ablation synthesis to create nanoparticles by impacting the target material. In a laser ablation experiment, metal atoms evaporate and are instantly solvated by surfactant molecules, forming nanoparticles in the solution**[30]**.

c. Sputtering method

The process of depositing nanoparticles on a surface by ejecting particles through ion collisions is known as sputtering. Typically, annealing comes after a thin layer of nanoparticles is deposited via sputtering. The substrate type, annealing temperature and time, layer thickness, and other factors influence the size and form of the nanoparticles **[32]**.

d. Thermal decomposition method:

Heat causes a compound's chemical bonds to break, resulting in thermal breakdown, an endothermic chemical process **[6]**. The decomposition temperature is the precise temperature at which an element undergoes chemical breakdown.The metal is broken down at particular temperatures through a chemical reaction that yields secondary compounds, which is how the nanoparticles are created **[30]**.

e. The arc discharge method:

The arc discharge method is capable of generating a range of nanostructured materials. Among the carbon-based materials produced using this technology are fullerenes, carbon nanohorns (CNHs), carbon nanotubes, few-layer graphene (FLG), and amorphous spherical carbon nanoparticles. This method holds great importance, especially in the production of fullerene nanomaterials.

- Bottom-up method

The bottom-up method, also called as the constructive method the method the build-up of material from atom to clusters to nanoparticles, is the antithesis of the top-down technique Bottom-up method includes Chemical vapor deposition (CVD), Sol–gel, spinning, pyrolysis and biological synthesis **[36]**.

a. Sol-gel method

The words "sol" and "gel" combine to form the term "sol-gel method." Sol is a colloidal material made up of solid particles floating in a liquid at all times. A big, solid molecule that dissolves in the solvent is called a gel. The majority of nanoparticles may be produced using this process, which is the most popular bottom-up technique because to its simplicity; metal oxides and chlorides are the most often employed main reactants **[33]**.

b. Spinning method

A spinning disk reactor is used to create nanoparticles by spinning. It is made up of a revolving disk that is housed inside a reactor or chamber where physical characteristics like temperature can be adjusted. The liquid, which consists of the feedstock and water, is pumped out while the disk rotates at various speeds. The technique of spinning disc processing creates

magnetic nanoparticles by fusing together atoms or molecules, which are then placed, gathered, and dried **[32]** .

c. Chemical Vapour Deposition (CVD)

Chemical Vapor Deposition: The deposition of a thin layer of gaseous reactants on a substrate. By fusing gas molecules, deposition is accomplished in a reaction chamber at a specific temperature. When the combined gas and the heated substrate come into contact, a chemical reaction takes place.Nanoparticles produced by CVD are extremely pure, consistent, robust, and hard. The disadvantages of CVD are the requirement of special equipment and the gaseous by-products are highly toxic **[32]**.

d. Pyrolysis

Pyrolysis stands as the predominant method employed across industries for large- scale nanoparticle production. In this process Precursor materials burn in this process using a flame. These feedstocks are fed into the furnace at high pressures through a small opening, where they are burned, whether they be liquid or vapor. In place of conventional flames, some furnaces use lasers and plasma to reach high temperatures for effective evaporation. Pyrolysis offers the advantages of simplicity, cost-effectiveness, and continuity, ensuring high yields throughout the process **[30]**.

e. Biological synthesis

In biological synthesis, plant extract and microorganisms like fungi and bacteria are used to create nanoparticles. Phytonanotechnology has demonstrated a new, easy, and affordable avenue for the manufacture of nanoparticles. The benefits of phytonanotechnology include scalability, biocompatibility, and the capacity to synthesize nanoparticles using water as a universal solvent and reducing agent.Various plant parts, including the root, fruit, stem, seed, and leaf, are used to create nanoparticles. It has been demonstrated that the formation of different kinds of nanoparticles is caused by organic acid, proteins, vitamins, and secondary metabolites like alkaloids, flavonoids, terpenoids, polysaccharides, and heterocyclic compounds.Microorganisms are thought to be vastly potential nanofactories **[30]**.

❖ **Plant extract**

Various plants and their extracts serve as sources for nanoparticle synthesis, utilizing different plant components including leaves, stems, roots, and fruits. These plants harbor biomolecules like carbohydrates, proteins, and coenzymes, which possess the capability to effectively reduce mineral salts into nanoparticles. The biological approach has been harnessed for synthesizing metal or metal oxide nanoparticles **[33]**.

❖ **Bacteria**

Bacteria possess the capability to reduce metal ions, making them valuable for nanoparticle synthesis. Various bacterial species are utilized in the synthesis of nanoparticles, including those involved in mineral and other innovative synthesis methods **[30]**.

- **Fungi**

The use of superoxide nanoparticles for fungi is a highly effective method with well-defined morphology. Due to the presence of an enzyme between cells, fungi act as a biological organism. Notably, fungi tend to yield a greater quantity of nanoparticles compared to bacteria **[30]**.

- **Yeast**

Yeast, single-celled microorganisms present in eukaryotic cells4, serve as the foundation for synthesizing numerous nanoparticles **[30]**.

I.6.4. Properties of Nanoparticles

Materials at the nanoscale behave differently from those of atoms and bulk materials. This divergence manifests across magnetic, optical, electrical, mechanical, chemical, and physical domains. Alterations in particle size directly influence their interactions with surrounding atoms, thereby modifying their overall behavior. When nanoparticles aggregate, their collective properties may diverge significantly from those of individual particles due to variations in shape and structure. The properties of nanomaterials are intricately linked to factors such as chemical composition, size, geometry, crystal structure, and surface characteristics **[37]**.

I.6.4.1. Physical properties of nanomaterials

By altering their dimensional sizes, metallic materials' melting point is one of their most significant physical attributes that is impacted. A bulk material's melting temperature is independent of its size, however because nanomaterials have unbounded surface atoms, its melting point lowers as particle size reduces. When a bulk substance is split into nanoscale components, its total volume stays the same, but its collective surface area grows. This leads to an increase in the surface-to-volume ratio at the nanoscale when compared to bulk materials. The molecules or atoms on the surface have a high surface energy and a tendency to group together**[33]**.

I.6.4.2. Chemical properties of nanomaterials

The chemical properties of nanomaterials include how they interact with the target material, how stable they are, how sensitive they are to environmental stimuli like heat, light, and moisture, and how they are affected by factors like flammability, corrosion, corrosion resistance, oxidation . In addition, nanomaterials frequently have unique or improved catalytic

properties, such as reactivity, selectivity, and catalysis, in comparison to their conventional analogs **[33]**.

I.6.4.3. Magnetic properties of nanomaterials

Increasing the strength, effectiveness and intensity of the magnet, as the smaller the size of the grains, the greater their magnetism .Nanomaterials are Magnetic properties are among the most important sources used in the manufacture of ship engines, ships and power generators electrical**[33]**.

I.6.5. Optical properties of nanomaterials

Optical properties include such as nanoparticle color, light penetration, and the absorption and reflection capabilities, and the absorption and reflection capabilities of ultraviolet rays in the solution or when Coated on the surface.

I.6.5.1. Electrical properties of nanomaterials

When the scale is reduced to the nanoscale, the quantum effect takes over; electron delocalization occurs along the axis of nanotubes, nanorods, and nanowires. Conducting materials behave as either semiconductors or insulators due to electron confinement, which causes the energy bands to be replaced by discrete energy states. This result indicates that the metal is becoming a semiconductor. Carbon nanotubes, for example, can be either semiconductors or conductors depending on their nanostructure. To reduce the diameter of the wire**[33]**.

I.6.5.2. Mechanical properties

Mechanical properties, such as elasticity, ductility, tensile strength, and resilience, are crucial factors shaping material applications. They significantly impact the enhancement of mechanical properties in nanomaterials, including hardness, yield strength, elasticity modulus, and toughness compared to bulk materials. This improvement in mechanical strength primarily stems from a decreased likelihood of defects and increased structural integrity. Additionally, it enhances the hardness and durability of alloys, as well as the super plasticity of ceramics**[33]**.

I.7. Iron and iron oxides

In recent years, there has been a growing interest among researchers in synthesizing and investigating nanoscale metal oxides for various applications. Plant extracts have garnered increasing attention, notably for their effectiveness and eco-friendliness in this process. These extracts contain numerous organic compounds, including flavonoids, carboxylic acids, phenols, and proteins, which facilitate the recovery of mineral substances and the facile production of nanoparticles. Iron oxide, in particular, stands out due to its diverse range of

applications.

I.7.1. Iron:

In the Holy Qur'an, it is stated, " *And We sent down iron, wherein is great might and benefits for mankind* " (Al-Hadid: 25). This Surah sheds light on the significance of iron in human life and the universe as a whole.

Iron is one of the four most abundant elements that make up the Earth's crust. It is considered the most important metal in human civilization, with a wide variety of applications. Iron is symbolized by the chemical element Fe, has an atomic number of 26, and an atomic weight of 55.845. Its electronic configuration is ([Ar] $4s^2$ $3d^6$) and it exhibits two stable oxidation states: +II and +III .The global annual production and use of iron is approximately one million tons. Iron is the most prevalent transition metal and has numerous practical applications. Iron-based materials are commonly used as magnetic adsorbents in water treatment processes. Using iron-based materials for wastewater treatment offers several advantages, including high reactivity, low cost, environmental friendliness, magnetic properties, and high adsorption capacity **[38]**.

I.7.2. Iron oxide:

On (Fe) exhibits notable chemical reactivity, readily forming compounds with surrounding elements, particularly oxygen (O) and water (H_2O). Various forms of iron oxide compounds have been identified, totaling sixteen types thus far. These compounds fall into two main categories: iron oxides and hydroxides. They distinguish themselves based on composition, the valence of the iron element, and notably, crystal structure. In contrast to pure iron, which is a conductive metal, iron oxides typically behave as semiconductors. Their conductivity tends to rise with elevated temperatures, unlike the behavior of pure iron, which can either conduct heat or serve as an insulator. Iron oxide (IO) has several uses in the energy and environmental sectors, but its use as a nano-adsorbent for the treatment of water and wastewater is a relatively new field of study**[38]**.

Table I.1: Forms of different iron oxide compounds.

Oxides	**Hydroxides**	**Oxide/hydroxide**
iron(II) oxide, wüstite(FeO) iron(II,III) oxide, magnetite (Fe_3O_4) iron(III) oxide (Fe_2O_3) alpha phase, hematite (α-Fe_2O_3) beta phase, (β-Fe_2O_3) gamma phase, magnetite (γ-Fe_2O_3) epsilon phase, (ε-Fe_2O_3)	iron(II) hydroxide ($Fe(OH)_2$) iron(III) hydroxide ($Fe(OH)_3$),(bernalite)	goethite (α-FeOOH) , akaganéite (β-FeOOH), lepidocrocite (γ-FeOOH), feroxyhyte (δ-FeOOH), ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$ approx.), or $5Fe_2O_3.9H_2O$, better recast as $FeOOH.0.4H_2O$ high-pressure FeOOH

I.7.3. Iron oxide nanoparticle:

Iron oxides exist in many forms in nature, with magnetite (Fe_3O_4), maghemite(γ -Fe_2O_3), and hematite (α -Fe_2O_3) being probably the most common. These three oxides are also very important technologically.

I.7.3.1. Magnetite (Fe_3O_4)

This mineral is one of the common iron oxides and one of the main iron ores Magnetite has an inverse spinel structure with Fe(III) ions distributed randomly between octahedral and tetrahedral sites, and Fe(II) ions in octahedral sites [39].

I.7.3.2. Hematite (α-Fe_2O_3)

Hematite, the earliest identified iron oxide, is prevalent in various rocks and soils. It is recognized by several names, including ferric oxide, red ochre, specularite, specular iron ore, kidney ore, or martite. Hematite exhibits a blood-red hue when finely divided, while it appears black or gray in coarse crystalline form. This mineral maintains remarkable stability under standard environmental conditions and frequently emerges as the ultimate product in the transformation of other iron oxide **[39]**.

I.7.3.3. Maghemite (γ-Fe_2O_3)

Maghemite possesses a spinel structure akin to magnetite, albeit with vacancies in the cation sublattice. In this structure, Fe (III) ions arranged in a regular pattern, with a vacant site following every two filled ones, occupies two-thirds of the sites. According to Haneda and Morrish, the extent of vacancy ordering diminishes as particle size decreases, with maghemite particles smaller than approximately 20 nm exhibiting no vacancy ordering creative**[39]**.

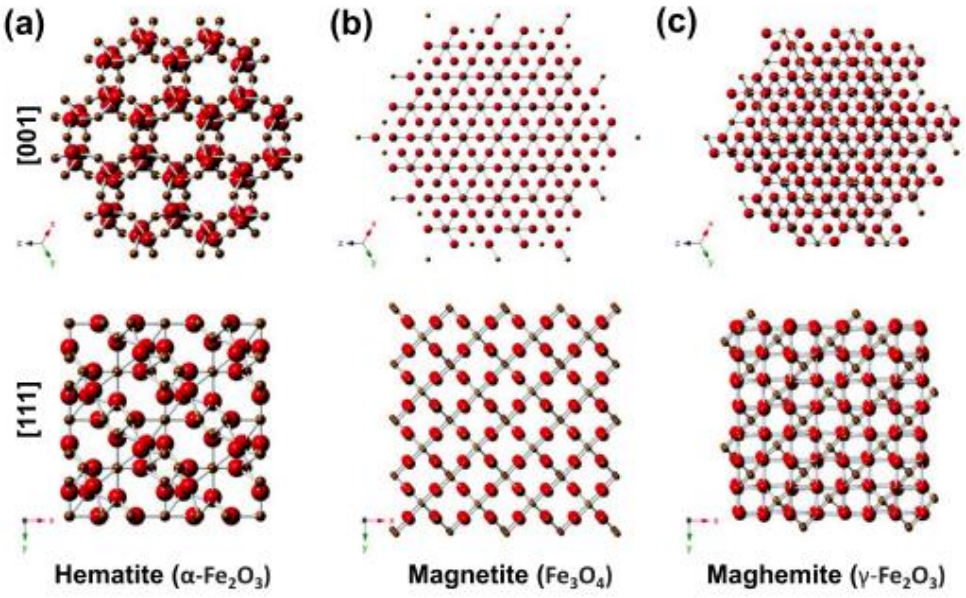


Figure I. 5: Crystal structure of a-Fe_2O_3, Fe_3O_4 and γ-Fe_2O_3**[38]**.

I.7.4. Physical and magnetic properties of iron oxides

The physical and magnetic properties of iron oxide are summarized in the table[40].

Table I.2: Physical and magnetic properties of iron oxides.

Property	**Hematite**	**Magnetite**	**Maghemite**
Molecular formula Density (g/cm3) Melting point (C)	α -Fe_2O_3 5.26 1350	Fe_3O_4 5.18 1583e1597	γ -Fe_2O_3 4.87 -5
Hardness	6.5	5.5	
Type of magnetism	Weakly ferromagnetic or antiferromagnetic	Ferromagnetic	Ferrimagnetic
Curie temperature (K)	956	850	820-986
MS at 300 K (A-m2/kg)	0.3	92-100	60-80
Standard free energy of formation DGf (kJ/mol)	742.7	1012.6	711.1
Crystallographic system	Rhombohedral, hexagonal	Cubic	Cubic or tetrahedral Defect spinel
Structural type	Corundum		P4332 (cubic);
Space group	R3c (hexagonal)	Inverse spinelFd3m a ¼ 0.8396	P41212(tetragonal)
Lattice parameter (nm)	a ¼ 0.5034, c ¼ 1.375 (hexagonal) aRh ¼ 0.5427, a ¼ 55.3 rhombohedral)		a ¼ 0.83474 (cubic);a ¼ 0.8347, c ¼ 2.501 (tetragonal)

I.7.5. Applications of iron oxide NPs

Iron oxide nanoparticles were chosen for their robust magnetic properties. They were first used in biology, and have subsequently been used in medicine, mainly for the magnetic separation of cells and biological products and for magnetically directing drug delivery systems to specific sites. These nanoparticles' size, charge, and surface chemistry all have a big impact on how widely they are distributed biologically. Due to its critical role in therapeutic and diagnostic approaches, magnetic carriers and particles have seen an increase in utilization in clinical applications over the past few decades. Magnetic nanoparticles have

garnered considerable attention as versatile materials across various scientific disciplines, especially in life sciences. Numerous potential applications for magnetic nanomaterials exist in several key scientific fields Applications of iron oxide nanoparticles were chosen for their robust magnetic properties. They were first used in biology, and have subsequently been used in medicine, mainly for the magnetic separation of cells and biological products and for magnetically directing drug delivery systems to specific sites. These nanoparticles size, charge, and surface chemistry all have a big impact on how widely they are distributed biologically. Due to its critical role in therapeutic and diagnostic approaches, magnetic carriers and particles have seen an increase in utilization in clinical applications over the past few decades. Magnetic nanoparticles have garnered considerable attention as versatile materials across various scientific disciplines, especially in life sciences. Numerous potential applications for magnetic nanomaterials exist in several key scientific fields the most important of which is water treatment. Iron oxide nanoparticles have demonstrated efficacy in eliminating a range of contaminants from water, including pesticides, heavy metals, and certain organic pollutants. Because of its unique qualities such as its enormous surface area and capacity to both chemically interact and absorb these pollutants **[41]**.

Conclusion:

To sum up, one of the most exciting areas of nanotechnology is nanomagnetism, which is creating new opportunities for cutting-edge uses in electronics, energy, data storage, and medicine. Controlling magnetic characteristics at the nanoscale can help devices function more efficiently,be smaller, and have more precision. Nanomagnetism technology is anticipated to make major contributions to advancements in numerous disciplines as research and development continue, underscoring its significance as a cornerstone of the scientific and technological future.

References

1. Balzani, V., *Nanoscience and nanotechnology: a personal view of a chemist.* small, 2005. **1**(3): p. 278-283.
2. Ratner, M.A. and D. Ratner, *Nanotechnology: A gentle introduction to the next big idea*. 2003: Prentice Hall Professional.
3. Abd, A.N., M.H. Hassoni, and M.H. Hasan, *Properties and biomedical applications of copper oxide nanoparticles.* Biochem. Cell. Arch, 2018. **18**(2): p. 1763-1766.
4. Andrieux-Ledier, A., *Elaboration de nanoparticules d'argent par réduction de sels métallo-organiques: contrôle de taille, stabilité, organisation et propriétés physiques*. 2012, Université Pierre et Marie Curie-Paris VI.
5. Majumder, D.D., et al., *Nano-materials: Science of bottom-up and top-down.* IETE technical review, 2007. **24**(1): p. 9-25.
6. Nel, A., et al., *Toxic potential of materials at the nanolevel.* science, 2006. **311**(5761): p. 622-627.
7. Baig, N., I. Kammakakam, and W. Falath, *Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges.* Materials Advances, 2021. **2**(6): p. 1821-1871.
8. Lagashetty, A. and A. Bhavikatti, *Nanotechnology-an overview.* Mater. Sci. Indian J. Rev, 2019. **5**: p. 274-276.
9. Singh, A., S. Dubey, and H.K. Dubey, *Nanotechnology: The future engineering.* Nanotechnology, 2019. **6**(2): p. 230-233.
10. Satyanarayana, T. and S.S. Reddy, *A review on chemical and physical synthesis methods of nanomaterials.* Int. J. Res. Appl. Sci. Eng. Technol, 2018. **6**(1): p. 2885-2889.
11. Szczyglewska, P., A. Feliczak-Guzik, and I. Nowak, *Nanotechnology–general aspects: A chemical reduction approach to the synthesis of nanoparticles.* Molecules, 2023. **28**(13): p. 4932.
12. Kargozar, S. and M. Mozafari, *Nanotechnology and Nanomedicine: Start small, think big.* Materials Today: Proceedings, 2018. **5**(7): p. 15492-15500.
13. Menéndez-Manjón, A., et al., *Nano-energy research trends: bibliometrical analysis of nanotechnology research in the energy sector.* Journal of Nanoparticle Research, 2011. **13**: p. 3911-3922.

14. Otero, R., F. Rosei, and F. Besenbacher, *Scanning tunneling microscopy manipulation of complex organic molecules on solid surfaces.* Annu. Rev. Phys. Chem., 2006. **57**: p. 497-525.
15. Yadav, V., *Nanotechnology, big things from a tiny world: a review.* AEEE, 2013. **3**(6): p. 771-778.
16. Ojha, G.P., et al., *Three-dimensionally assembled manganese oxide ultrathin nanowires: Prospective electrode material for asymmetric supercapacitors.* Energy, 2019. **188**: p. 116066.
17. Kang, D., G.P. Ojha, and H.Y. Kim, *Preparation and characterization of nickel nanoparticles decorated carbon fibers derived from discarded ostrich eggshell membranes for supercapacitors application.* Functional Composites and Structures, 2019. **1**(4): p. 045004.
18. Prasad, R., A. Bhattacharyya, and Q.D. Nguyen, *Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives.* Frontiers in microbiology, 2017. **8**: p. 1014.
19. Forster, S.P., S. Olveira, and S. Seeger, *Nanotechnology in the market: promises and realities.* International Journal of Nanotechnology, 2011. **8**(6-7): p. 592-613.
20. Chaudhri, N., G.C. Soni, and S. Prajapati, *Nanotechnology: an advance tool for nano-cosmetics preparation.* Int. J. Pharma Res. Rev, 2015. **4**(4): p. 28-40.
21. Abdulazeem, L., et al., *Nanoparticles in cosmetics, what we don't know about safety and hidden risks. A mini review.* Glob. NEST J., 2022. **25**: p. 1-5.
22. Mu, L. and R.L. Sprando, *Application of nanotechnology in cosmetics.* Pharmaceutical research, 2010. **27**: p. 1746-1749.
23. Kaul, S., et al., *Role of nanotechnology in cosmeceuticals: a review of recent advances.* Journal of pharmaceutics, 2018. **2018**.
24. Chandrakala, V., V. Aruna, and G. Angajala, *Review on metal nanoparticles as nanocarriers: Current challenges and perspectives in drug delivery systems.* Emergent Materials, 2022. **5**(6): p. 1593-1615.
25. Ramsden, J.J., *Nanotechnology for military applications.* Nanotechnology Perceptions, 2012. **8**(2): p. 99–131-99–131.
26. Alkandari, A., Z. Almesri, and S. Moein, *Nanotechnology Applications: an Analytic Comparison.* Journal of Advanced Computer Science and Technology Research, 2017. **7**(2): p. 67-80.

27. Street, A., et al., *Nanotechnology applications for clean water: solutions for improving water quality*. 2014: William Andrew.
28. Goutayer, M., *Nano-émulsions pour la vectorisation d'agents thérapeutiques ou diagnostiques: étude de la biodistribution par imagerie de fluorescence in vivo*. 2008, Université Pierre et Marie Curie-Paris VI.
29. Keghouche, N. and B.D. Eddine, *Elaboration et etude de nanoparticules Au/TiO2 et Ag/TiO2*. 2017.
30. Ijaz, I., et al., *Detail review on chemical, physical and green synthesis, classification, characterizations and applications of nanoparticles.* Green Chemistry Letters and Reviews, 2020. **13**(3): p. 223-245.
31. Kumari, S. and L. Sarkar, *A review on nanoparticles: structure, classification, synthesis & applications.* Journal of Scientific Research, 2021. **65**(8): p. 42-46.
32. Ealia, S.A.M. 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. IOP Publishing.
33. Mekuye, B. and B. Abera, *Nanomaterials: An overview of synthesis, classification, characterization, and applications.* Nano Select, 2023. **4**(8): p. 486-501.
34. Barhoum, A., et al., *Review on natural, incidental, bioinspired, and engineered nanomaterials: history, definitions, classifications, synthesis, properties, market, toxicities, risks, and regulations.* Nanomaterials, 2022. **12**(2): p. 177.
35. Habiba, K., et al., *Fabrication of nanomaterials by pulsed laser synthesis.* Manufacturing nanostructures, 2014. **10**: p. 263-292.
36. Arole, V. and S. Munde, *Fabrication of nanomaterials by top-down and bottom-up approaches-an overview*. J. Mater. Sci, 2014. **1**: p. 89-93.
37. Shahzadi, P., *Properties of Nanomaterials and Environment*, in *Nanotechnology Applications in Environmental Engineering*. 2019, IGI Global. p. 28-43.
38. Keshta, B.E., et al., *State of the art on the magnetic iron oxide Nanoparticles: Synthesis, Functionalization, and applications in wastewater treatment.* Results in Chemistry, 2024: p. 101388.
39. Simeonidis, K., et al., *Inorganic engineered nanoparticles in drinking water treatment: a critical review.* Environmental Science: Water Research & Technology, 2016. **2**(1): p. 43-70.

40. Teja, A.S. and P.-Y. Koh, *Synthesis, properties, and applications of magnetic iron oxide nanoparticles.* Progress in crystal growth and characterization of materials, 2009. **55**(1-2): p. 22-45.

41. Ali, A., et al., *Synthesis, characterization, applications, and challenges of iron oxide nanoparticles.* Nanotechnology, science and applications, 2016: p. 49-67.

CHAPTER II

Generalities about the menthe plant

Introduction

Plant is the main economical and effective source for nanoparticle synthesis. Studies indicate that some Medicinal herbs and natural products, which are generally used by people, have biological and natural properties and pharmaceutical effects.

Since medicinal herbs do not have harmful chemical effects, but rather have beneficial effects against any pathogens and bacteria, in addition to the possibility of using them as a disinfectant, antiviral, antioxidant and antimicrobial agent. Many studies have been conducted on a range of medicinal plants such as mint, which is considered a green synthesis using biocompatible agents **[1]** .

II.1. Definition of menthe plant

Mint is a perennial herb with very fragrant, toothed leaves and tiny purple, pink, or white flowers. There are many varieties of mintall fragrant, whether shiny or fuzzy, smooth or crinkled, bright green or variegated. However, you can always tell a member of the mint family by its square stem. Rolling it between your fingers, you'll notice an aromatic scent and think of candy, sweet teas, or even mint juleps **[2]**.

II.2.Classification and etymology

II.2.1. Etymologies

The vertices (en, a grappe, crisp, crepue, or parfois romaine) for my latin mentha spicata heads or viridis L. The origin of the men that was retrouve in the Greek mythology, il existe deux versions of this history: - Hades (date of the nèbres) fait la cour à la nymphe menthè, so the woman should change the plant. It is not possible to use the frame as normal, because it does not work normally. He said: Men and Pluton's eyes; Pluton to protect the woman from changing the plant. We have a Greek name called "minthe" or Latin "mentha" and a special sign in the text.

II.2.2. Classic classification

Table II.1: Classic classification

Mentha
Mentha longifolia
Scientific classification
Kingdom: Plantae
Division: Magnoliophyta
Class: Magnoliopsida
Order: Lamiales
Family: Lamiaceae
Genus: ***Mentha*** L.

Mentha is a genus of about 25 species (and many hundreds of varietiesof flowering plants in the family Lamiaceae (Mentha Family). Species within Mentha have a subcosmopolitan distribution across Europe, Africa, Asia Australia, and North America. Several mint hybrids commonly occur.

II.3. Formal description of mentha

II.3.1. Leaves

The leaves are opposite persistent, subsessile, lanceolate, sharp, saw-toothed, green on both sides, glabrous or almost glabrous. The implantation of the leaves is paripinnate and decussate (with an angle of 90°).

II.3.2. Flower

The flowers grow in a cluster in the leaf axil. They are zygomorphic and hermaphroditic. The flowers are pink or lilac, in sparse terminal spikes, long, slender, linear-acute; calyx bracts and teeth linear, glabrous or ciliate; pedicels and calyx tube glabrous; corolla glabrous inside; ovoid carpels. The flower has a bract which extends beyond the floral parts, the flower is pentamerous oligostemonous and its petals are fused (gamopetalous). Flower formula: (5S)+((5P)+4E)+(2C) The ovary is great.

II.3.3. Inflorescence

The inflorescence is indefinite in a dense cylindrical spike.

II.3.4. Stem

The stem of spearmint is said to be quadrangular (square) ascending (orthotropic). It is purple in color. The size of spearmint can reach a maximum height of 1.20 meters but on average varies between 0.30 and 0.60 cm the stems are glabrous or glabrescent, branched. Spearmint is a plant with creeping rhizomes.

II.3.5. Racines

La racine est une racine pivotante qui dure plus de 3 ans. On les trouve en dessous de chaque pied, des rhizomes (tiges souterraines) servent à la propagation de la plante.

Figure II.1: "A picture of the parts of a manthe plant" **[3]**.

II.4. Extraction of volatile oil

Steam distillation is a method used to extract the volatile oil of the peppermint plant, which was described in the British Pharmacopoeia of 1958, where a device is used to extrac"clevenger" light oil. When drying the samples, 50 grams are taken and placed in a volumetric flask and 400 ml of ordinary water is added. The distilled oil is separated using a separating funnel. According to two stages in the presence of ether, the upper sample is taken and the ether is evaporated using a rotary evaporator device .The oil is obtained, which must be placed in a sealed bottle at a temperature of 4° in the refrigerator until the tests to be diagnosed are performed **[4].**

II.4.1. Identification of a number of active compounds of both types of peppermint oil using gas-liquid chromatography "GLC"

Use this technique to estimate qualitatively and quantitatively. In the leaves of menthe plants of all kinds, as a precise and specialized method for separating them, diethyl ether is used as a solvent to dilute the volatile oil samples, and then by injecting 1µ of it, its active compounds are identified based on the retention time values (Rt) for each compound and then compared to the retention time values of standard compounds, according to reference to the separation conditions as shown in "Table 2".

Table II.2: The condition of separating gas-liquid chromatography for volatile oils in the leaves of Menthe spicata & Menthe piperita [4].

100 C°	Primary temp. of column
250 C°	Final temp. of column
5 C°/min	Temp. height average
300 C°	Detector temperature
4min\ml	gas C
3m×1/8 inch	Internal diameter
1 µl	On column injection
3% SE-30	Liquid phase
Mesh 120-100 (Teflon)	Solid phase
1 Mv	Attenuation
FID	Flame ionization detector

II.5. Propriétés pharmacologiques de M. spicata

The essential oils and extracts of M. spicata present in its biological properties and different pharmacological methods, such as essential medicines. This may cause a potent acaricide and can be used to protect against it tetranychus turkestani, which is the cause of 100% of the deaths of adults at this time concentration de 20 µL/L.

Table II.3: Chemical compounds in Menthe genus and their pharmacological properties**[6]**.

Pharmacological Properties	Chemical Compounds Responsible for Pharmacological Properties.
Antioxidant	Ascorbic acid, Rosmarinus acid, δ-terpinene, α-terpinene, p-cymene, 1,8-cineole, ciscarveol, carvone, Rosmarinus acid, cynaroside, cryptochlorogenic acid, naringin.
Antibacteria	Luteolin, Rosmarinus acid, caffeic acid, gallocatechin, epigallocatechin gallate, catechins, menthone, isomenthone, hexadecenoic acid, cis-carveol, carvone, limonene.
Antifungal and Anti Yeast	Limonene, piperitenone oxide, menthol, menthone, carvone, cis-carveol and carvone, piperitone, citronellal, caffeic acid, naringin, cryptochlorogenic acid, Rosmarinus acid.
Antivira	Menthol, eriocitrin, Rosmarinus acid, luteolin 7-O-rutinoside, hesperidin, phytol.
Anticancer	Eugenol, caryophyllene, t-cadinol, menthone, menthol crotonate, naringin, cryptochlorogenic acid, rosmarinic acid.

II.6. The economic and nutritional importance of menthe plants

Menthe is one of the plants that cannot be dispensed with. It is used in the kitchen fresh or dried, and also in the preparation of various types of salads, tea, juices, sweets and ice cream. As for the extraction aspect, it is in the form of oil extracted from it and is found in the manufacture of many commercial products. Such as toothpaste, chewing gum, candy, dairy products, soft drinks, spices, mouthwash solutions, cosmetics, and peppermint oil is added to some medications to give them an acceptable taste.

The menthe plant contains a group of nutrients, such as fiber, proteins, carbohydrates, fats, vitamins and mineral acids. It also contains a group of mineral salts, including magnesium, zinc, calcium, sodium and iron **[7]**.

References

1. El Menyiy, N., et al. (2022). "Medicinal uses, phytochemistry, pharmacology, and toxicology of Mentha spicata." Evidence-Based Complementary and Alternative Medicine 2022.

2. Naureen, I., et al. (2022). "Chemical composition and therapeutic effect of mentha species on human physiology." Scholars Bulletin 8(1): 25-32.

3. http://galerneau.pierre.free.fr/Labo_Ouvert/pdf/mentha_spicata.pdf

4. H Al-Hashemy, F., et al. (2013). "THE EFFECT OF NITROGEN FERTILIZATION AND SPRAYING OF GIBBERELLIC ACID & ALGAMIX ON THE QUALITY AND QUANTITY ON SOME ACTIVE CONSTITUENTS FROM OIL OF MENTHA PIPERITA & MENTHA SPICATA." Mesopotamia Journal of Agriculture 41(3): 19-36.

5. https://di.univ-blida.dz/jspui/bitstream/123456789/29730/1/219%20M.BVP.pdf

6. https://saudijournals.com/media/articles/SB_81_25-32.pdf

7. Wami, S. A., et al. (2022). "Menthe: A review on its bioactive compounds and potential health benefits." Quality Assurance and Safety of Crops & Foods 14(4): 154-168.

CHAPTER III

Generalities about adsorption.

Introduction

Over the pasts several decades, rapid population, social and cultural expansion changing rich lifestyles and resource use and continuous advances in industry and technology have been accompanied by intensive modernization and urban growth. With the growing have exacerbate the degradation of many ecosystem and seriously thraetend human health and the environment strict rules and regulation on the emission of pollutants from industrial waste streams have been issued by various regulatory bodies.At the same time, advanced research has been conducted through the invention of a wide range of treatment technologies, the most important of which is adsorption process, which is basic approach widely, used in wastewater treatment processes mainly on the basis of its simplicity economic feasibility, technical feasibility and social acceptability **[1]**.

III.1. Adsorption phenomenon

Adsorption is a spontaneous physical or chemical process, influenced by the relationship process, influenced by the relationship between the properties of the absorbing substance (solid), and requires specific conditions of pressu and temperateur this process is accompanied by a change in free energy (∆G)and a decrease in entropy (∆S) , as the movement of particles is restricted due to their attachment to the surface of the absorbed substance, resulting in a decrease in heat energy (∆H) according to the known thermodynamic relationship **Eq.(1)**:

$$\Delta G° = \Delta H° - T\Delta S° \qquad \textbf{Eq.(1)}$$

III.2. Importance of adsorption

Although the adsorption process is considered an old technique, it still occupies a prominent place in a wide range of industries and applications in the current era. It is used in various industries such as petroleum, dyes, and food, including cooking oils and dairy products, and there are many other uses that cannot be enumerated**[2]**.

The adsorption process is particularly used to carry out many separation operations, especially those that are difficult or impractical to accomplish using traditional methods such as distillation, absorption, or membrane systems.

One of the most common applications of the adsorption process is in the treatment and purification of water, especially that which arises from various industrial processes and sewage. This process aims to remove any toxic pollutants harmful to the environment and society, in addition to treating the color, taste, and odor resulting from pollution.

These applications have facilitated tremendous technological advancement in the preparation and provision of a diverse range of effective materials. This, in turn, has

contributed to achieving many important applications in adsorption processes for various purposes .

Researchers have attempted to articulate a clear concept of the mechanism by which adsorption occurs. This endeavor has led to the development of various mathematical equations that express this phenomenon.

Nowadays, it has become possible to solve these mathematical equations related to the adsorption process using numerical analysis. Furthermore, advancements in software and the availability of advanced equipment have allowed us to directly determine and study the factors influencing adsorption without the need for shaded areas**[3, 4]**.

III.3. Types of adsorption

Based on the intermolecular bonds between the adsorbate and the adsorbent surface, which result in specific forces depending on the nature of the materials involved, this process can be divided into types: physical adsorption and chemical adsorption **[5]**.

III.3.1. Physical adsorption

Physisorption, also known as van der Waals adsorption, is characterized by the presence of natural attraction forces between the surface of the solid material, which is typically inactive due to the electronic saturation of its atoms, and the molecules or ions being adsorbed. This cohesion occurs as a result of the bonds formed between those atoms and molecules, leading to the formation of partial layers on the adsorption surface and this type occurs at low temperatures **[6, 7]**.

III.3.2. Chemical adsorption

This is the result of the association of discrete molecules with the surface of a material through the formation of bonds that include covalent, ionic, or coordinative bonds, or a mixture of these types. This type of adsorption requires high activation energy, typically ranging from 20 to 200 kcal/ mo**l [8, 9]**.

III.4. Comparision of chemical and physical adsorption

The following table expresses the difference between the two types of adsorption **[10]**.

Table III.1: Comparative table showing the difference between types of adsorption Haut du formularies.

	Physical adsorption	Chemical adsorption
Types of bonds	**BondsVan Der -Weels**	**Bonds chimical**
Process temperature	**is relatively low compared to the boiling point of the adsorbent**	**is very high compared to the boiling point of the adsorbent**
Individuality of molecules	**Preservation of individuality of molecules**	**Destroying the uniqueness of molecules**
Désorption	**Easy**	**Difficult**
kinetics	**Fast and independent of heat**	**Very slow**
Heat of adsorption	**Weak**	**Veryheg**
Energies involved	**Between (40-400)k cal / mol**	**40 k cal / mol**
Types of training	**Multilayer and single-layer configuration**	**Single-layer configuration**

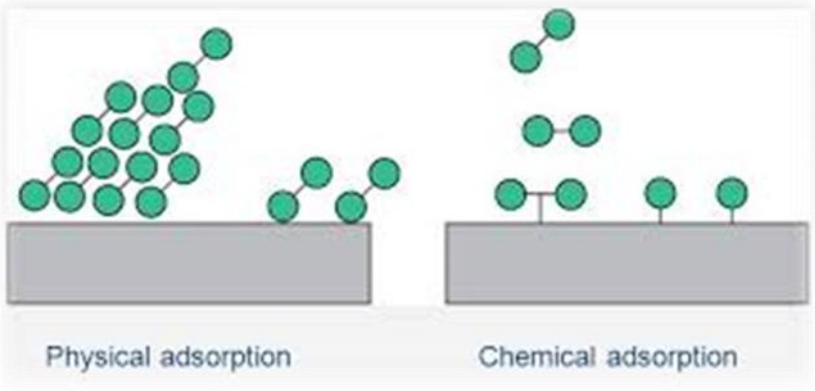


Figure: III. 1 Shows the difference between physical adsorption and chemical adsorption**.**

III.5. Adsorption Principle

The mass transfer of molecules occurs from the fluid phase towards the center of the adsorbent. This process takes place within a grain of adsorbent. Adsorbent materials have large specific surfaces, typically developed on industrial porous materials. During the adsorption of a chemical species such as a molecule from a polluted aqueous solution**[11]**

The transfer from the liquid phase to the solid phase occurs in several stages that can be defined as follows **[2]**:

- External diffusion: This corresponds to the transfer of the solute (molecules from the liquid or gas phase) within the solution at the external surface of the adsorbent. The transfer of matter depends on the flow of liquid over the surface of the adsorbent.
- Internal diffusion: Liquid molecules penetrate inside the pores. Diffusion depends on the concentration gradient of the solute .
- Surface diffusion: This corresponds to the fixation of particles on the surface of the adsorbent pore

It is at the end of these stages that the element to be adsorbed reaches the adsorption site where it is effectively retained, depending on the binding force that is established (physisorption or chemisorption).Adsorption is an exothermic process, which means it occurs with the release of heat, leading to heating of the solid and a reduction in the amounts adsorbed **[12]**.

III.6. Adsorptions mechanism

The applications of adsorption in life are many, including the removal of organic contaminants from water. This process occurs through physical and chemical forces, resulting in several adsorption mechanisms, the most important of which are:

III.6.1. Van der Waals forces

Van der Waals forces are a type of mechanism that occurs between atoms and molecules as a result of low-intensity electrical disturbances. These disturbances lead to the generation of an attractive dipole, which is important in the adsorption of organic pollutants, a process known as ion-exchange adsorption **[13]**.

III.6.2. Coulombforces

Coulomb forces are the electrostatic forces that occur as a result of a change in pH and affect the surface functional groups of the adsorbent. A difference in charge between these groups and the adsorbent occurs as a result of deprotonation, protonation or enantiomeric substitution of the surface functional groups. These forces are considered electrostatic, and adsorption is more common in ionised organic molecules and inorganic ions. This is known as electrostatic attraction **[14]**.

III. 6.3. Hydrogen bonds

It forms a bond between molecules, bond between a less electrosalient atom and a more electrosalient atom also known as electron pair adsorption **[15]**.

III.7. Factors affecting the adsorption phenomenon:

The phenomenon of extortion is influenced by several factors, the most important of which are:

III.7.1. Effect of temperature

Temperature is one of the crucial factors in the adsorption process. At low temperatures, physical adsorption occurs, and as the temperature increases, adsorption shifts from physical to chemical, accomplished by an increase in the adsorption of molecules on the solid surface. Additionally, adsorption is exothermic, highlighting the significance of temperature in the adsorption process **[16]**.

III.7.2. Effect of pH

The acidity of the solution affects the adsorption process by influencing both the adsorbate and adsorbent material, as well as the solvent. This is manifested through the competition between the adsorbate material, the adsorbent surface, and the solvent for hydroxide (OH^-) and hydrogen (H^+) ions. Therefore, it has either a positive or negative impact on the adsorption process, as well as on the adsorption isotherms and the amount or capacity of the adsorbate material on the adsorbent surface, varying from one compound to another**[16]**.

III.7.3. Specific surface

The surface area of the adsorbent is directly related to the number of active sites on it. As the surface area increases, the number of active sites also increases, leading to an increase in adsorption capacity. Therefore, surface area is a crucial factor in the adsorption process**[8, 17]**.

III.8. Concentrastion of adsorbent

Increasing the concentration of the adsorbate results in an increase in the rate of mass diffusion and transfer on the adsorbent surface. This diffusion enhances the adsorption capacity**[9]**.

III.8.1. Time equilibrium

It is the period of time in which the concentration of the solution stabilizes and then decreases an equilibrium occurs between the adsorbent and the desorbent , and this may take hours , days , or even weeks**[16]**.

III.8.2. Shaking speed

The speed of shaking contributes to the distribution of the adsorbent on the adsorbent surface so that it gives maximum adsorption , this is important factor in the adsorption procès **[18]**.

III.8.3. Nature of the adsorbent

The adsorption process is affected by the physical and chemical properties of the adsorbent, and the adsorption increases with the increase in the molecular mass of the adsorbent and the presence or absence of effective polarized groups in its structure, as well as the solubility of the adsorbent in different solvents. The lower the solubility of the adsorbent, the greater the adsorption capacity, these factors have a role in determining the interaction between the surface of the adsorbent and the efficiency of adsorption, and this difference in characteristics leads to spontaneous adsorption, especially in multicomponent systems**[19]**.

III.8.4. Dimentions of pores

The adsorption efficience also depends on the size of the pores and their distribution on the surface, as the surface area has a great influence on the adsorption process. The large the surface area, the s'aller the size of the pores and minutes of the adsorbent, resulting in an increase in the active sites on the surface of the adsorbent, which ultimately leads to an increase in adsorption**[19]**.

III.9. Adsorption isotherm

Isotherm is a graph that relates the amont of adsorbent to the concentration of the substance in solution at equilibrium., which describes the adsorption process, as this graph is obtained from the results of tests conducted at a certain time and at a constant temperature, and to calculate the amount of adsorbent, the following equation is used the following equation**[20]** Eq.(2):

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \textbf{Eq.(2)}$$

$\mathbf{C_0}$: Initial concentration of the adsorbent (mg/L).

$\mathbf{C_e}$: The concentration of the adsorbent in solution at equilibrium (mg/L).

V: Volume of the adsorbent (liters).

m :Mass of the adsorbent (g).

$\mathbf{q_e}$:quantity of adsorbent (mg/g).

Some of the most important adsorption isotarm models that describe theadsorbent–adsorbate interactions include the Friendlich model Timken's model and Longmire's model**[20]**.

III.9.1. The Freundlich model

This model is a descriptive equation that treats adsorption on solid heterogeneous multilayer surfaces layers, which is expressed by the following mathematical equation **[21]**Eq. (3):

where :

$$q_e = k_f C_e^{1/n} \qquad \textbf{Eq.(3)}$$

$\mathbf{q_e}$:the amount of adsorbent at equilibrium (mg/g).

$\mathbf{k_f}$:is a constant related to the adsorption capacity.

$\mathbf{C_e}$:Adsorbent concentration at equilibrium (mg/g).

n:heterogeneity factor.

k_f relates to the adsorption capacity, while n/1 relates to its density at where **[22]**.

n=1: the adsorption is linear; there is no interaction between the adsorbed species.

- 1 < n/1: Adsorption is good, new adsorption sites appear.

- 1 > n/1: Adsorption is not good, weak adsorption bonds.

The Freundlich isotherm applies to adsorption processes occurring on inhomogeneous surfaces and this isotherm gives an expression defining the surface inhomogeneity and the exponential distribution of active sites and their energy**[11]**.

III.9.2. Longmire's model

This model is a theory proposed by the scientist Longmire's in 1918, the adsorption of the solute

on a solid, which is a simple model based on several assumptions, including**[23]**.

- Only one monomolecular layer is formed on the solid.
- All active sites are equivalent.
- Each site can adsorb only one molecule of the solute, monolayer adsorption.
- There are no interactions between the adsorbed molecules.

Expressed by the following equation **[24] Eq. (4)**:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \times k_l} + \frac{C_e}{q_{max}} \qquad \textbf{Eq.(4)}$$

Where:

C_e: adsorbent concentration at equilibrium (mg/L).

K_l: Longmire's equilibrium constant (mg/L).

q_e: quantity of adsorbent at equilibrium (mg/g).

q_{max}: Maximum adsorption capacity (mg/g).

Longmire's isotarm properties are determined by the separation factor R_L **[24]**(Eq5):

$$R_l = \frac{1}{1 + k_l C_0} \qquad \textbf{Eq. (5)}$$

Where if:

$R_l = 0$: non-reversible adsorption**.**

$R_l = 0$: linear adsorption.

***R_l*<1** : good adsorption conditions.

***R_l*>1** : adsorption conditions are not good.

The Longmire's adsorption model is mainly used to describe solid phase adsorption to determine and compare the adsorption capacity of different adsorbents and the Langmuir isotherm represents the surface coverage by balancing the relative rates of adsorption and dynamic equilibrium **[19]**.

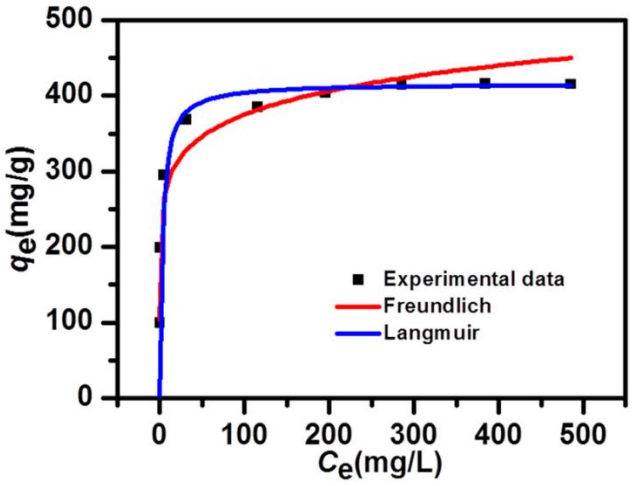


Figure III 2: Curve representing Longmire and Freundlich's quantum adsorption model in terms of concentration

III.9.3. Temkin model

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage . As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed qe against lnCe and the constants were determined from the slope and intercept. The model is given by the following equation **[11]** **(Eq6)**

$$q_e = \frac{RT}{b} + \ln (A_T + C_e)$$

$$q_e = \frac{RT}{b_T} + \ln A_T + \left(\frac{RT}{b}\right) \ln C_e$$

$$B = \frac{RT}{b_T}$$

$$qe = B \ln AT + B \ln Ce \qquad \textbf{Eq. (6)}$$

A_T=Temkin isotherm equilibrium binding constant (L/g)

b_T = Temkin isotherm constant

R=universal gas constant (8.314J/mol/K)

T= Temperature at 298K.

B = Constant related to heat of sorption (J/mol).

From the temkin plot shown the following values were estimated: A_T =1.075 L/g, B=25.34J/mol which is an indication of the heat of sorption indicating a physical adsorption process and the R^2=0.62.

III.10. Adsorption kinetics

Adsorption kinetics describes the rate of retention or release of an adsorbent from an aqueous solution to a solid phase interface. In adsorption, linear or non-linear kinetic analysis is applied. A goodness-of-fit index is applied to determine which model best describes the process. The following models **[25]**can ascertain the kinetics of adsorption on the surface of the adsorbent:

III .10.1. Pseudo-First Order Model

The model considers the rate of change thatthat occurs in the adsorption of the adsorbent at a given reaction timea given reaction time is directly proportional tothe difference in concentration and the rate at whichremoval of the adsorbent over time is expressed as **[25](Eq7**):

$$\frac{dq_t}{dt} = K_t\,(q_e - q_t) \qquad \textbf{Eq. (7)}$$

Where:

$\mathbf{q_e}$: Is the adsorption capacity of the adsorbent at equilibrium (mg/g).

$\mathbf{q_t}$: Is the adsorption capacity of the adsorbent at time t (mg/g).

$\mathbf{K_t}$: Is the rate constant for pseudo first order adsorption (min^{-1}).

After equation **Eq. (7)** is integrated and boundary conditions are applied, t = 0 to t = t and q_t = 0 to q_t = q_e the integrated form of the equation Eq. (7) becomes:

$$\log(q_e - q_t) = \log(q_e) \frac{k_1}{2.303} \cdot t \qquad \textbf{Eq. (8)}$$

III.10.2. Pseudo-Second Ordre Model

In this model, the speed of the reaction is related to the amount of material adsorbed on the surface of the adsorbent and the amount adsorbed at equilibrium and is expressed by the following kinetic equation**[25]**Eq.(9):

$$\frac{dq_t}{dt} = k_2\,(q_e - q_t)^2 \qquad \textbf{Eq. (9)}$$

k_2:is the rate constant of the pseudo second order adsorption ($g.mg^{-1}.min^{-1}$). The integrated form of the equation for the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_e becomes **Eq.(10)** :

$$\frac{t}{q_t} = \frac{1}{(k_2 - q_e^2)} + \frac{t}{q_e} \qquad \textbf{Eq. (10)}$$

III.10.3. Intra-particle diffusion

The diffusion mechanism can be explained using the intraparticle diffusion model. Intraparticle diffusion usually depends on various factors such as the physical properties of the adsorbent, the initial concentration of the solution, the temperature, and the rotational speed in the batch mode of the adsorbent. The intraparticle diffusion equation, proposed by Weber and Morris, can be expressed as follows **Eq. (11)**:

$$q_t = K\, t^{0.5} + C \qquad \textbf{Eq.(11)}$$

Where **q** is the adsorbed quantity of solute, **K** is the intraparticle diffusion parameter and **C** is the thickness of the boundary layer. A plot of q versus **t** would give a straight line if intraparticle diffusion were the limiting process **[26]**.

Conclusio:

Separation of substances using adsorption techniques and isotherm models is an effective way to purify water and improve its quality. These techniques are based on the physical and chemical properties of the materials intended for separation, where adsorbents or complexes are used that interact with harmful substances and impurities in the water.

Adsorption technology relies on the ability of adsorbents to absorb harmful compounds from water, while isotherm technology separates substances using temperature differences and chemical balances in thesystem.Using these technologies, water quality is significantly improved by removing harmful organic and inorganic substances, such as heavy metals, harmful chemicals, and harmful bacteria. These technologies are also used to improve the taste and odour of water, providing water suitable for human and industrial use. Overall, adsorption and isotherm technologies are emerging as reliable and effective options for water treatment, contributing to improving public health and effectively preserving the environment.

References

1. Foo, K.Y. and B.H. Hameed, Insights into the modeling of adsorption isotherm systems. Chemical engineering journal, 2010. 156(1): p. 2-10.
2. Adamson, A.W. and A.P. Gast, Physical chemistry of surfaces. Vol. 150. 1967: Interscience publishers New York.
3. Adrar, I., Utilisation des noyaux de dattes pour l'elimentation des ions fe2+ en solution aqueuse. 2016, UMMTO.
4. Meullemiestre, A., Valorisation des déchets de la filière «bois» en deux étapes: isolation des molécules extractibles puis fabrication de charbon actif: cas du pin maritime. 2014, Université de La Rochelle.
5. Mechrafi, E., Adsorption, désorption et mobilité des herbicides au contact des adsorbants organiques et minéraux. Doctorat, Université Mohammed V–AGDAL, Rabat, Maroc, 2002.
6. Benamraoui, F., Elimination des colorants cationiques par des charbons actifs synthétisés à partir des résidus de l'agriculture. 2018.
7. Bouaziz, A., Biosorption du nickel par la biomasse Pleurotusmutilus. Ecole Nationale polytechnique, 2009.
8. De Berg, K.C., The kinetic-molecular and thermodynamic approaches to osmotic pressure: A study of dispute in physical chemistry and the implications for chemistry education. Science & Education, 2006. 15: p. 495-519.
9. Tsai, W., et al., Adsorption of basic dyes in aqueous solution by clay adsorbent from regenerated bleaching earth. Applied Clay Science, 2005. 29(2): p. 149-154.
10. Clark, R.M. and J.Q. Adams, Evaluation of BAT for VOCs in drinking water. Journal of environmental engineering, 1991. 117(2): p. 247-268.
11. Dada, A., et al., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of applied chemistry, 2012. 3(1): p. 38-45.
12. Ho, Y. and G. McKay, Kinetic model for lead (II) sorption on to peat. Adsorption science & technology, 1998. 16(4): p. 243-255.
13. Yuh-Shan, H., Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics, 2004. 59(1): p. 171-177.
14. Wang, L. and A. Wang, Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorillonite. Journal of hazardous materials, 2008. 160(1): p. 173-180.

15. Sedira, N., Etude de l'adsorption des métaux lourds sur un charbon actif issu de noyaux de dattes. MAGISTER En chimie physique et analytique, Option: Environnement et traitement des eaux, université Mohamed Chérif Massaadia Souk-Ahras, 2013: p. 45.

16. Bentahar, Y., Caractérisation physico-chimique des argiles marocaines: application à l'adsorption de l'arsenic et des colorants cationiques en solution aqueuse. 2016, Université Côte d'Azur (ComUE).

17. Tawfeeq, I.M. and A.J. Mohammed, Adsorption Ability and Kinetic of (Congo Red, Methyl Green) Dyes on Iraqi Siliceous Rocks. Journal of Global Pharma Technology, 2009. 11(07).

18. Toole, A.P. and D.G. Crosby, Environmental persistence and fate of fenoxaprop-ethyl. Environmental Toxicology and Chemistry: An International Journal, 1989. 8(12): p. 1171-1176.

19. Kiselev, A. and V. Khopina, Influence of properties of adsorbent, and of the surface and bulk solutions on adsorption from solution. Transactions of the Faraday Society, 1969. 65: p. 1936-1942.

20. GUESMIA, S., L'adsorption des colorants (bleu de methylene et chrome iii) sur la bentonite. 2015.

21. Pathania, D., S. Sharma, and P. Singh, Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. Arabian journal of chemistry, 2017. 10: p. S1445-S1451.

22. GHALI, S., ÉTUDE DE LA CARBONISATION D'UN PRÉCURSEUR VÉGÉTAL,LES NOYAUX D'OLIVES. UTILISATION DANS LE TRAITEMENT DES EAUX. 2008.

23. Mar, K., et al., Comparison of Arsenic adsorption on lignite, bentonite, shale, and iron sand from Indonesia. Procedia Earth and Planetary Science, 2013. 6: p. 242-250.

24. Allahdin, O., Élimination (par adsorption sur la brique activée) de polluants métalliques dans les eaux de la République Centrafricaine et les pays en voie de développement: Aspects texturaux, physicochimiques,(électro) cinétiques et thermodynamiques. 2014, Lille 1.

25. Tóth, J., Uniform interpretation of gas/solid adsorption. Advances in colloid and interface science, 1995. 55: p. 1-239.26.Chekem, C.T., Matériaux carbonés multifonctionnels à porosité contrôlée à partir des ressources végétales tropicales: application au traitement de l'eau par photocatalyse. 2017, Université de Perpignan.

CHAPTER IV

Methods and materials

Introduction

In this experiential chapter, we review water treatment materials and methods that are an essential part of improving water quality and preserving the environment.We will focus on analysing and evaluating experimental materials and technologies. The objective is to provide a comprehensive and reliable understanding of these technologies and materials and how they can be effectively used in water treatment to achieve the goals of sustainability and low cost.

IV.1. Geographical location of the sample

El Oued is located in the south-east of Algeria , bordered to the north by states of Tébessa ,Khenchla and Biskra ,to the south are the states of Ouargla and Biskra, to west are the states of Djelfa ,Ouargla and Biskra , and to the east by Tunisia.The state of El Oued is considered one of Algerian states with a primarily agricultural character due to the diversity of agriculturale crops in it and the cultivation of mint is an important agricultural activity in the state ofn El Oued , as its farms enjoy a suitable climate and fertile soil that makes it an ideal home for the cultivation of this plant .

The sample used in this study was taken from Gumar region, which is located in the north of the state and whose location is shown below .

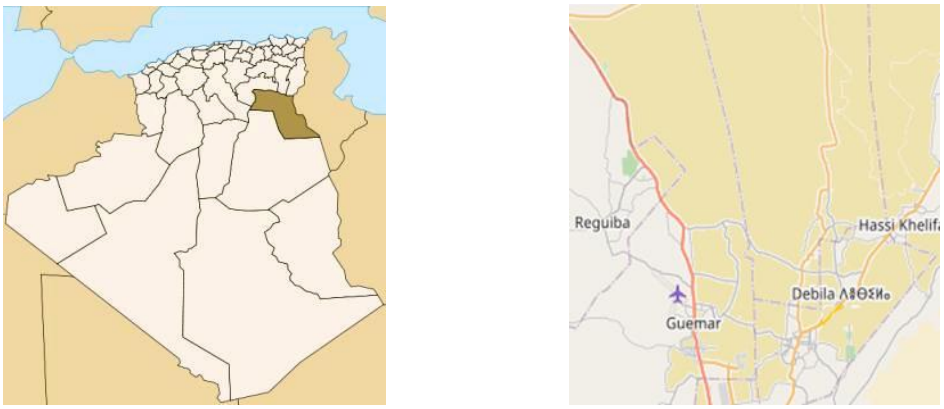


Figure IV.1 : The geographical location of El Oued State and El Oued State Guemar Department.

IV.2. Preparation of samples

This study used mentha plants, harvested from the city of Gambar. The mint leaves were collected and washed with distilled water. The rinsing process was repeated several times. Then they were dried in a dry place for 10 days. Then they were ground with an electric grinder into a fine powder, and stored in a glass container free of moisture.

IV.3. Devices and used materials

We organise all the materials, equipment and glassware used in the experimental protocol in the following table:

Table IV.1: Laboratory equipment used in the experimental protocol.

Devices	Model
UV	SP-UV 300 SRB
SEM	Phenomprox Phenom WORLD
X-ray	AXRD Benchtop PROTO
FTIR	Agilent Technologies Cary 630 FTIR
Centrifuges	SCILOGEX SCI412
pH meter	Consort multi parameter analyse C3010
Sensitive balance	OHAUS / EXPLORER
Heat plate and Magnetic mixer	Dlab MS –H-S
Drying oven	Elds Haet
Incinerator	Nabertherm 30-3000°C

Table IV.2: Chemicals and their sources.

Chemicals	N°	The source
Ethanol	04-2319457610-43	DORIZU OPTIMUM SOLUTIONS SPAIN
Méthanol	213032500	BIOCHEM CHEMOPHARMA FRANCE
$FeCl_3$	B-7705-08-0-03-11-011	BIOCHEM CHEMOPHARMA FRANCE
NaOH	B1310-73-2-0109-011	BIOCHEM CHEMOPHARMA FRANCE
HCl	V3N459023N	CARLO ERBA FRANCE
Acetone	201272500	BIOCHEM CHEMOPHARMA FRANCE
Acetic acid	12A250509	VWR PROLABO FRANCE
Methyl orange Sodium4[(4dimethylamino)phenyldiazenyl]benzene sulfonate	1065109	HONEYWELL FLUKA SPAIN
Methylene blue -bis(Dimethylamine)-phenothiazin-5-ium-3,7chloride	24.3201603	BIOCHEM CHEMOPHARMA FRANCE
Congo red disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato naphthalen2yl)diazenylphenyl]phenyl]diazenylnaphthalene1-sulfonat	403050100-0917-011A	BIOCHEM CHEMOPHARMA FRANCE

Crystal violet 4-{Bis [4(dimethylamino) phényle] méthylène}-*N*, *N*-dimethylcyclohexa-2,5-dien-1-iminium chloride	403220025/0100	BIOCHEM CHEMOPHARMA FRANCE

Table IV.3: Laboratory glassware used in the protocol.

Laboratory glassware	Volume
Becher	1000 /50/25 ml
Volumetric flask	1000/250/100 ml
Reund bottom	250/500 ml
Graduated cylinder	100/5 ml
Funnel	/
Conical flask	500ml
Pipeett	1/2/5/10ml
Laboratory glass bassin	150/180 mm

IV.4. Extraction method

An ethanol extraction method was chosen, where 50 g of dried plant material and 300 ml of ethanol were placed for 24 hours with continuous shaking using a magnetic stirrer. It is then filtered using filter paper **[1] (Reference [1] was based on it with some modifications)**.

IV.5. Preparation of nanoparticles iron oxide

We prepared a solution of $FeCl_3$, its concentration C = 0.04 M and its volume V = 100 ml, then we shook it and heated it until it reached the temperature is 70°C, then we add 50ml of mint extract, and continue shaking while heating for an hour.At a temperature of 70°C.

We put the obtained solution in the centrifuge for 10 minutes at 5000 t/min. We put the sediment collected from the centrifuge in the Becher. We put this sediment to dry in the oven for 24 hours at a temperature of 100 °C.

We grind the dry sediment into small pieces using a mortar mash, then burn the sediment after it dries in the oven under a temperature of 550°C for an hour **[1](Reference [1] was based on it with some modifications)** .

IV.6. Green Synthesis

The pilot green synthesis protocol for nanosynthesis was carried out in phases as shown in the following scheme.

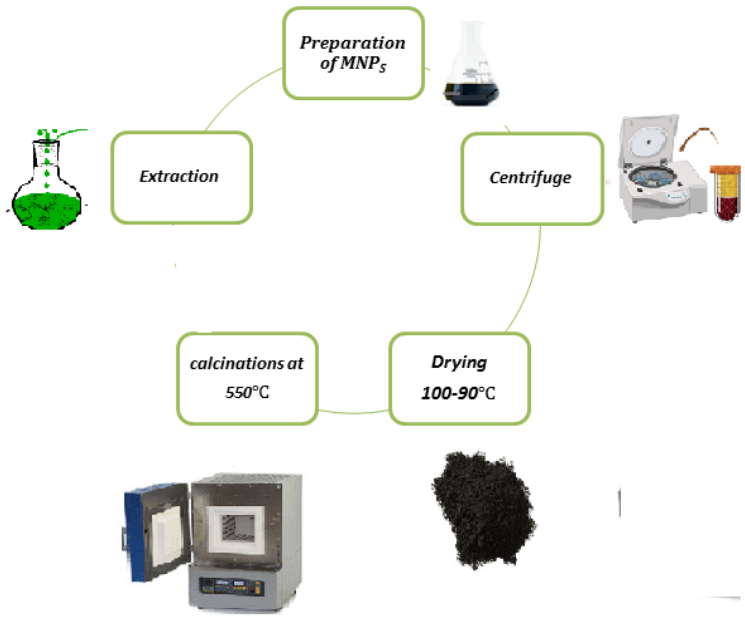


Figure IV.2 : Green synthesis of nanoparticles.

The green synthesis process was conducted through sequential stages to obtain nanoparticles applicable in the treatment of polluted water. This process involves utilizing a botanical source for the extract and a mineral solution of specific concentration and proportions. These procedures occur under controlled and predetermined temperature conditions.

IV.7. Characterization techniques

IV.7.1. Analysis and description techniques

This study was conducted to investigate the properties of the plant extract **[2]**.Iron oxide nanoparticles were produced from plant extracts through an environmentally friendly procedure involving the localised reduction of NPs and characterisation was performed using UV spectroscopy, band gap energy Eg , FTIR, SEM, molecular and atomic structure determination by x-ray , The pH was also measured at zero point(pHz) **[3]**.

IV.7.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The transmission technique does not require a separate accessory. The user simply places sample directly into the infrared (IR) beam. As the IR beam passes through the sample, the transmitted energy is measured and a spectrum is generated. However, the analyst must often prepare the sample into a pellet, mull, film etc. before the transmission measurement can be made. This requires expertise and can be time consuming **[4]**.We characterised 3 different adsorption regions via the vibrational modes of the ligands present in nanoparticles prepared from $FeCl_3$ surface alkyl baskets (2800-3000) and cm^{-1} –COO group (900-1800) cm^{-1} Fe-O bonds (800-400) cm^{-1} **[5]**.

IV.7.1.2. Ultraviolet-visible adsorption specteroscopy

Derivative spectrophotometry is a highly useful analytical technique for extracting qualitative and quantitative information from spectra consisting of unresolved bands, and for removing the effect of baseline shift and baseline slope. It consists of calculating and plotting a mathematical derivative of a spectral curve. Thus, the information content of a spectrum is presented in a more useful form, providing a convenient solution to a number of analytical issues, such as analysing multicomponent systems, removing sample turbidity, matrix background, and enhancing spectral detail. Derivative photometric spectrophotometry isnow an affordable standard feature in modern UV/VIS spectrophotometry **[6]**.

IV.7.1.3. X-ray diffraction (XRD)

X-ray crystallography is the experimental science that determines the atomic and molecular structure of a crystal by scattering a beam of incident X-rays in several specific directions.By measuring the angles and intensities of these scattered rays, a crystallographer can produce a three-dimensional image of the density of electrons within the crystal**[4]**. The lattice structure of the prepared iron nanoparticles was obtained by analysing X-ray diffraction (XRD) **[7]**.

IV.7.1.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most important tools for analysing the microscopic properties of nanomaterials and the main reason for the advantage of SEM in examining the nanostructure is the high resolution that can be obtained. Thus, SEM has been an important tool in screening SEM analysis helps us to determine the structure of the bonding of additives with iron nanoparticles **[5]**.

SEM gives magnified images of the size, shape, composition, crystallinity and other physical and chemical properties of a sample. SEM's material and surface sciences are magnified many times to see surface structures and assess surface variations The opportunity to analyse the material to be examined using an electron beam generated in a vacuum environment, and filtered by electromagnetic lenses in the same position to create a high-resolution image **[8]**.The images in the microscope are created by calculating the reflections or reflected electrons from the interaction of the electron beam with the material Images of the surface and pores of the Fe_2O_3 nanomaterial were obtained by SEM FOV: 95.9 μm, mode: 15 kV - detector point: SED.

IV.7.2. Study of sample charge

The pH value at the zero charge point (pHz) of the sample was studied within a range of pH (10 – 5) using pre-prepared solutions of NaOH and HCl at a concentration of 0.01 molar.

25 ml of these solutions were added to a beaker with a volume of 50 ml, and the acidity level was adjusted at each value within the studied range. Subsequently, 25 mg of nanospheres were added. The pH_i value was measured, and the samples were left in the magnetic stirrer for 24 hours, after which the pH_f value was measured. The difference in the value (ΔpH) was calculated for each value within the studied range, and $\Delta pH=0$ was obtained within the studied range.

IV.8. The studied dys

IV.8.1. Dye selection test

We tested Nano's ability to adsorb the four dyes by preparing 4 solutions of the dyes (MB, CV, MO and CR) at a concentration of 25mg/l .25ml of each solution was placed in a 50 ml aliquot and 25 mg particles of each aliquot were shaken with a magnetic shaker for 3 hours in the dark.The methylene blue (MB) dye was chosen from among Congo red (CR), methyl orange (MO) and crystal violet(CV) for the ability of iron nanoparticles to absorb it in light, dark and uv light.

IV.8.2. Prepare the titration soulution

IV.8.2.1. Preparation of mother solution

In order to prepare the mother solution of concentration 50mg/l we weigh 50mg of methylene blue dye and dissolve it in water, use a 1000 ml calibrator, add water to the calibrator line and shake well.

IV.8.2.2. Determine experimental value of maximum wavelength of dye

We make several dilutions starting from the parent solution 50 mg/L and put each sample of the diluted solutions in a UV apparatus and scan in the field shown, which expresses the maximum wavelength found of $\lambda max = 664$ nm , and then plot the absorbance curve in terms of concentration to obtain the equation of the curve for methylene blue from the figure:

$$\mathbf{A = aC - b}$$

Where:

A = Absorbent

C = Concentration (mg /L)

a , b = Equation coefficients.

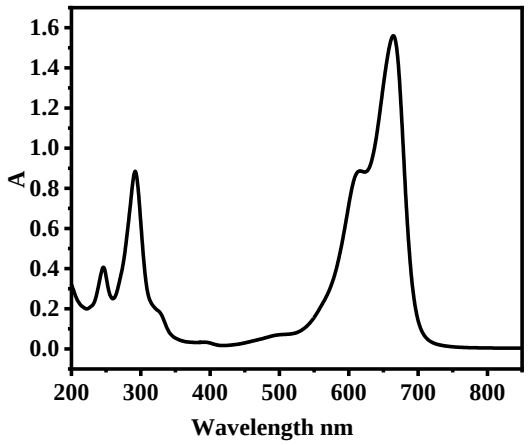


Figure IV.3: Maximum wavelength curve for methylene blue

IV.9. Applicatoin water treatment

IV.9.1. Photodegradation experiments

Ultraviolet (UV) water teratment is a process that user light to purify water from contaminats,this process relies on the use of light to stimulate chemical reaction that lead to the breakdown or oxidantion of organic materials and other pollutants, UV radiation is an effiectife and environmentally ferindly technologey ,as it does not requier the addition of chemicals it is widely used in drinking water treatment plants and for treating polluted water.

- **Experience of photodegradation in daylight**

We prepare a methylene blue solution at a concentration of 10 mg/l, pour 4 ml of the solution into a 25 ml Becher bottle with 4 mg of iron nanoparticles and leave it in daylight facing the sun. We start each time by measuring the UV absorbance from 30 to 350 minutes consecutive hours to measure the decrease in concentration after centrifugation of the sample and nanoseparation (using the maximum wavelength of methylene blue to read the absorbance values) **[9]**. After recording the final absorbance values, we plot the absorbance curve in terms of time to observe the decrease in dye concentration due to the adsorption phenomenon and the phenomenon can be traced by calculating the yield with the following relationship:

$$R = (A_0 - A_t) / A_0 \cdot 100 \ldots\ldots(*)$$

IV.9.2. Experiences of extortion in the dark

Prepare a methylene blue solution at a concentration of 10 mg/l pour 4 ml of the solution into a 25 ml Becher bottle with 4 mg of iron nanoparticles and shield it from light completely. Start each time by measuring the UV absorbance from approximately 30 to 350 minutes measure the decrease in concentration after centrifugation of the sample and separation of the

nanoparticles. After recording the absorbance results obtained, we can calculate the yield with the relationship labeled**(*)**above.

IV.9.3. Photodegradation UV experiment

The photolytic adsorption experiments were carried out by using a UV apparatus wavelength 365nm ,under UV emission as previously carried out in the preparation of methylene blue solution 10 mg/l and the nanoparticles were pre-weighed 4 mg, put 4 ml of the solution in each 25 ml beecher with the nanoparticles and turn on the UV light and make sure the distance of the light and each beecher is equal for all samples.Start the timer from 5 minutes to 350 minutes and take out each sample at the specified time to read the absorbance via UV after separating the solution from the nano via centrifugation.After recording all the absorbance values for all the samples, we calculate the permanent yield with the relationship **(*)** R % curve can also be plotted in terms of time.

IV.10. Adsorption modelling experiments

The adsorption experiments were modelled using a statistical analysis model in which the effect of three variables on adsorption (pH, contact time and amount of adsorbent) was studied, expressed as 17 possible experiments with 3 variables .

Modelling of the adsorption data was performed at room temperature in batch mode using 50 ml of Bicher, 10 mg/L methylene dye solution and continuous magnetic shaking.

IV.10.1. Effect of pH

In order to study the effect of solution pH on adsorption, the range of (4 -10) was chosen and the acidity of the solutions was adjusted using (NaOH/ HCl) and an optimum pH=7.

IV.10.2. Effect of the amount of material

Different amounts of (NPS) were used, ranging from 25-100 mg, and a mass of 62.5 mg was chosen as the optimal intermediate mass.

IV.10.3. Effect of contact time

Studying the effect of contact time (30 -120) minutes and 75 min as a medium value.

IV.11. Statistical Analysis Model

A statistical analysis model for water treatment by adsorption aims to study and analyze the impact of multiple variables on the process of adsorbing pollutants in water and the efficiency of their removal using adsorbent materials. These variables may include pH level, contact time between the adsorbent and the adsorbate, and the quantity of adsorbent used.

Firstly, the experiment is designed appropriately, where different levels of each variable are chosen and arranged randomly or systematically according to the experimental design. Then, data is collected from these experiments with high precision.Next, the data is analyzed

using statistical methods such as regression analysis to determine the relationship between the different variables and the efficiency of adsorption. Other statistical analysis tools such as Analysis of Variance may be used to estimate the effect of each variable and determine whether there are statistically significant differences between the levels of the variables.Subsequently, a statistical model is developed to accurately describe the relationship between the different variables and the efficiency of adsorption. This model can be used to predict the efficiency of adsorption under new conditions or to improve the conditions of the current process.Finally, the results are analyzed and interpreted, and they are used to improve adsorption-based water treatment processes, thus contributing to improving water quality and protecting the environment.

IV.12. Ruse of nanopartical adsorbent

✓ In all previous experiments, the nanomagnetic block used in each experiment was separated and rinsed several times using centrifugation.

✓ The block was dried in a drying oven at a temperature of 150°.

✓ The nano was reapplied several times under the same conditions in successive adsorption experiments and was confirmed to be effective in removing the dye.

✓ This process aims to reuse the adsorbent and exploit its full dye removal capabilities, making it a good candidate for several applications in commercial journals in particular.

IV.13. DPPH free radical inhibition test

The DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical inhibition test is a common method used to evaluate the antioxidant activity of compounds. The DPPH assay is based on the reduction of the DPPH radical, a stable free radical, by antioxidants**[10]**.The DPPH radical has a deep violet color with an absorption maximum at 517 nm.When an antioxidant donates an electron or hydrogen to DPPH, the color fades and the change in absorbance can be measured spectrophotometrically **[11]**.

The percentage of DPPH radical inhibition is calculated using the following formula:

$$\text{Inhibition (\%)} = ((A_{control} - A_{sample}) / A_{control}) \times 100$$

Where:

- $A_{control}$ is the absorbance of the control (DPPH solution with methanol)
- A_{sample} is the absorbance of the test sample (DPPH solution with the antioxidant)

The method of work

- **Preparation of DPPH Solution**

A DPPH solution is prepared by dissolving 2 mg of diphenylhydrazyl in 50 ml of methanol of a concentration we obtain a dark violet solution .

- **Preparation of Test Sample**

We prepare several different concentrations of the artificial sample diluted in methanol, and we take 1 ml from each concentration and add Add 1 ml of DPPH. We homogenize the solution and leave it for 30 minutes in the dark, after which the reading is performed at a wavelength of $\lambda max=517nm$

- **Measurement**

Measure the absorbance at 517 nm using a UV-Vis spectrophotometer. Lower absorption at 517 nm indicates higher antioxidant activity. The RC_{50} value is inversely proportional to the antioxidant power; A lower RC_{50} value indicates a stronger antioxidant.

Conclusion

In conclusion, the pilot chapter highlights ongoing efforts in improving water quality through the use of innovative technologies such as nanosynthesis, adsorption and photocatalysis. Thanks to these efforts, the results are remarkably promising in removing contaminants and improving water qualities. However, it is important to note that these methods need to be further studied and optimised to ensure their efficiency and environmental and health safety in the future.In short, the experimental chapter paves the way for further discoveries and developments in the field of water treatment, fuelling hope for a cleaner water future and better health for the environment and society.

References

1.Saleh, A.K., et al., Green synthesis and characterization of aluminum oxide nanoparticles using Phoenix dactylifera seed extract along with antimicrobial activity, phytotoxicity, and cytological effects on Vicia faba seeds. Biomass Conversion and Biorefinery, 2023: p. 1-17.

2.Shafey, A.M.E., Green synthesis of metal and metal oxide nanoparticles from plant leaf extracts and their applications: A review. Green Processing and Synthesis, 2020. **9**(1): p. 304-339.

3.Velasco, A., et al., Recent trends in graphene supercapacitors: from large area to microsupercapacitors. Sustainable Energy & Fuels, 2021. **5**(5): p. 1235-1254.

4.Cao, Y., et al., Influence of phytochemicals on the biocompatibility of inorganic nanoparticles: a state-of-the-art review. Phytochemistry Reviews, 2017. **16**: p. 555-563.

5.Abdullah, J.A.A., et al., Green synthesis and characterization of iron oxide nanoparticles by pheonix dactylifera leaf extract and evaluation of their antioxidant activity. Sustainable Chemistry and Pharmacy, 2020. **17**: p. 100280.

6.Li, G.-C., et al., Disambiguation and co-authorship networks of the US patent inventor database (1975–2010). Research Policy, 2014. **43**(6): p. 941-955.

7.Singh, J., et al., 'Green'synthesis of metals and their oxide nanoparticles: applications for environmental remediation. Journal of nanobiotechnology, 2018. **16**: p. 1-24.

8.Jana, J., M. Ganguly, and T. Pal, Enlightening surface plasmon resonance effect of metal nanoparticles for practical spectroscopic application. RSC advances, 2016. **6**(89): p. 86174-86211.

9.Kiew, P.L., et al., Iron oxide nanoparticles derived from Chlorella vulgaris extract: Characterization and crystal violet photodegradation studies. Progress in Energy and Environment, 2023: p. 1-10.

10. Benzie, I. F., & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. Analytical biochemistry, 239(1), 70-76.

11. Dhull, S. B., Kaur, P., & Purewal, S. S. (2016). Phytochemical analysis, phenolic compounds, condensed tannin content and antioxidant potential in Marwa (Origanum majorana) seed extracts. Resource-Efficient Technologies, 2(4), 168-174.

CHAPTER V

Presentation and discussion of results.

This chapter provides a comprehensive overview of the adsorption capacity of iron oxide nanoparticles in treating water contaminated with organic pollutants. It first explains physic-chemical analysis including X-ray diffraction, FTIR, and others. Secondly selecting suitable pollutant to take as an example for the rest of the study .Third, photocatalytic experiments with synthesized iron oxide nanoparticles .Finally studying the experimental conditions that affect the adsorption (removal) yield and choosing the optimal conditions that give the highest yield.

V.1. Study of the physicochemical properties of the synthesized nanoparticles

V.1.1. FTIR spectroscopy

FTIR analysis was performed to determine the quality and quantity of chemical bonds present in iron oxide nanoparticles before and after calcination.

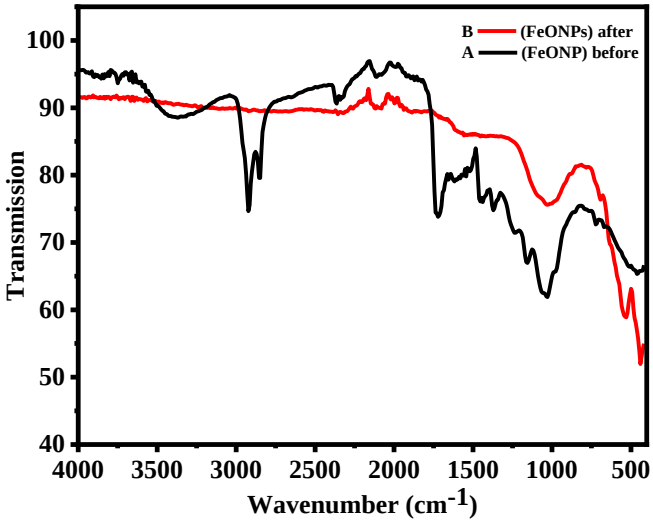


Figure V.1: FTIR spectrum of (A) before (B) after calcination iron oxide NPs.

a. The resulting infrared spectrum, both before and after calcination, shows a number of bands that indicate the presence of different functional groups.

b. The following observations were made prior to calcination, as shown in **Figure 1(A)**:

✓ A broad band of absorption between 3000 and 3500 cm^{-1} was seen, suggesting vibration linked to the (O-H) bond of either phenol or alcohol **[1]**.

✓ Absorption band in the range2920 cm^{-1} with the stretching vibrations(C-H) of the methyl group.

✓ Absorption band at 1720 cm^{-1} that represents stretching vibrations C=O **[2]**.

✓ There is also an absorption band at 1030 cm^{-1} indicating (C-O) Alcohol, ester groups Carboxylic acids and ethers **[3]**.

✓ Recording absorption bands between 1020 cm^{-1} and 2100 cm^{-1} is evidence of the presence of both bonds (C-N, C≡C and C-C) **[4]**.

✓ The wave band between 430 and 500 cm^{-1} shows the presence of inorganic peaks, which cross over stretching vibrations (Fe-O) **[5]**.

c. The FTIR spectrum of iron oxide nanoparticles after calcination was compared to spectrum 1(B), which revealed that the peaks of the organic compounds had diminished and vanished, along with the peak of the (O-H) bond, which spans the wave range of 3000-3500cm^{-1}.However, it is noted that the absorption band stays within the 400–500 cm^{-1} range, suggesting Fe–O vibration **[5]**.

V.1.2. X-ray diffraction (XRD)

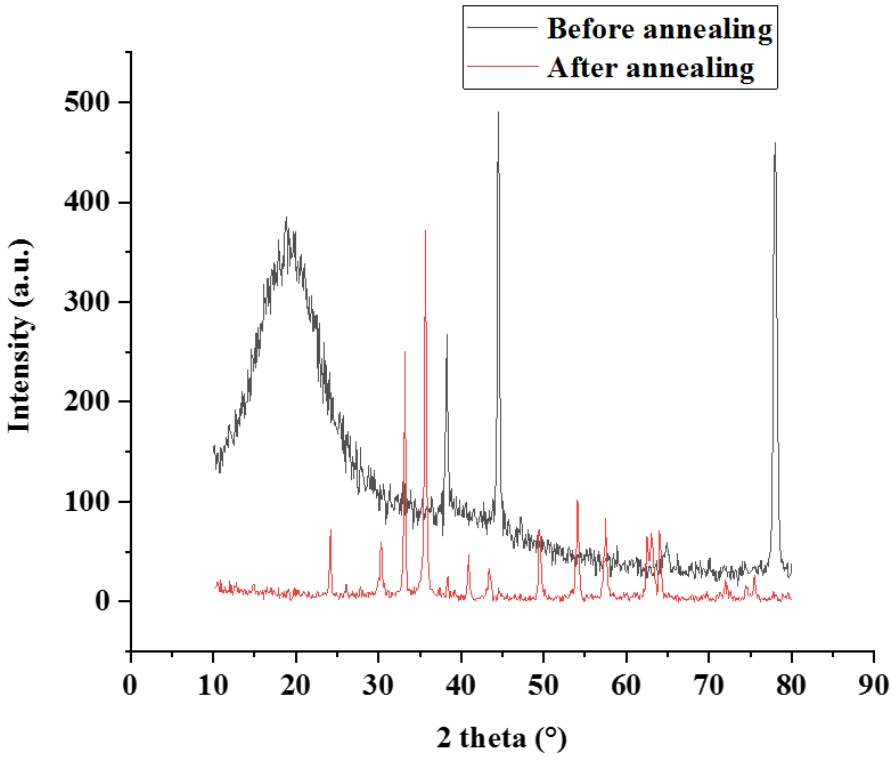


Figure V.2: The provided XRD pattern shows the diffraction data for the magnetic iron nanoparticles (NPs) before and after annealing. Here's a detailed explanation based on the XRD patterns:

1. **Before Annealing**:

- The pattern shows broad peaks with lower intensities.
- Broad peaks typically indicate smaller crystallite sizes and possible amorphous or poorly crystalline nature of the nanoparticles.
- Peaks observed at specific 2θ values can be attributed to the characteristic planes of the iron oxide phases (such as magnetite, Fe_3O_4).

2. **After Annealing**:

- The pattern after annealing shows sharp and well-defined peaks.

- This indicates improved crystallinity and larger crystallite sizes due to the annealing process.

- The increase in peak intensity and decrease in peak width suggest that the nanoparticles have undergone grain growth and a reduction in lattice strain.

- The presence of well-defined peaks matches well with the standard diffraction patterns of iron oxides, confirming the phase purity and enhanced crystalline nature post-annealing.

Specific Analysis:

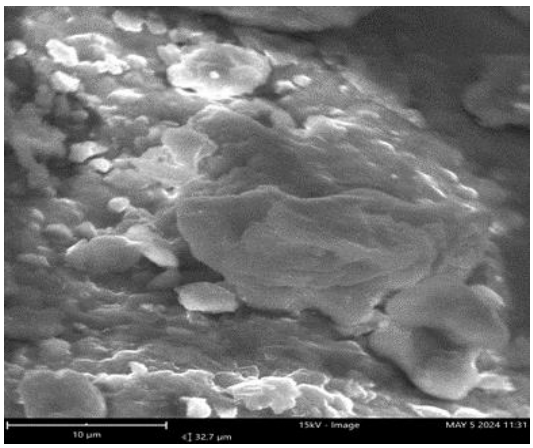
- The primary peaks of interest can be matched against standard diffraction patterns of iron oxides (such as Fe_3O_4 or γ-Fe_2O_3) to confirm the phases present before and after annealing.

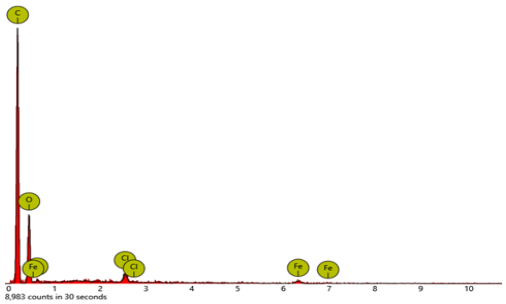
- **Before Annealing**: The broad peak around $2\theta = 35°$ is characteristic of Fe_3O_4 (magnetite) or γ-Fe_2O_3 (maghemite).

- **After Annealing**: The sharper peaks correspond to well-crystallized phases of iron oxides, typically Fe_3O_4 or α-Fe_2O_3 (hematite) depending on the annealing temperature and conditions.

The comprehensive XRD analysis of magnetic iron nanoparticles for water treatment demonstrates several key findings that align with existing studies and suggest the sustainability of the synthesized nanoparticles. Initially, the nanoparticles exhibit broad peaks, particularly around $2\theta = 30°$, 35°, and 57°, indicating a less crystalline structure. Upon annealing, these peaks become sharper and more defined, particularly at $2\theta = 30°$, 35°, 43°, 57°, and 63°, corresponding to the (220), (311), (400), (511), and (440) planes of Fe_3O_4, respectively. This improvement in crystallinity and structural stability is consistent with other research, which highlights the benefits of thermal treatment in enhancing the performance of iron oxide nanoparticles **[6]**.

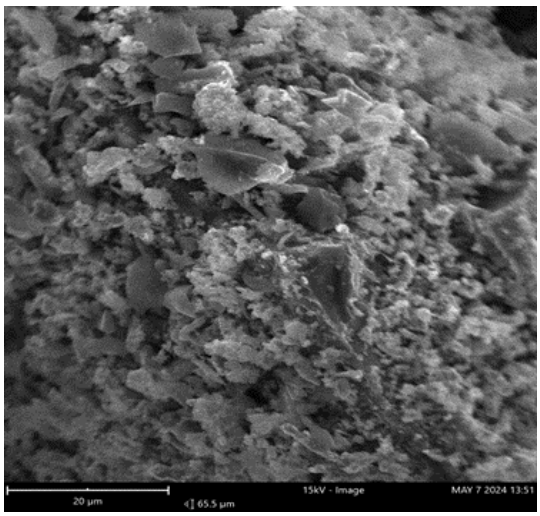
V.1.3. Scanning electron microscopy (SEM) and Energy dispersive x-ray detector (EDX)

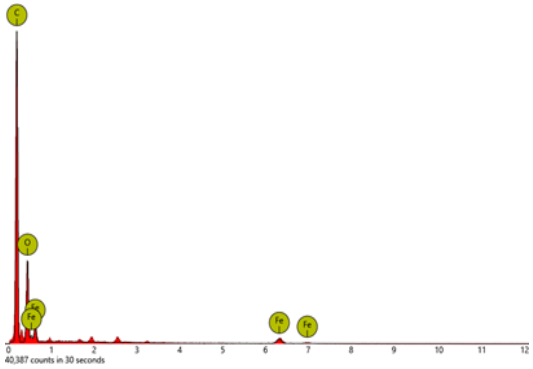




Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	72.04	64.22
8	O	Oxygen	26.82	31.84
26	Fe	Iron	0.62	2.59
17	Cl	Chlorine	0.51	1.35

(a)





Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	71.48	63.44
8	O	Oxygen	27.56	32.58
26	Fe	Iron	0.96	3.98

(b)

Figure V.3: Scanning electron microscopic images of Iron NPs powders: (a) before, (b) after calcination and EDX of treated samples.

Before calcination

The SEM image shows the iron NPs in a more irregular and agglomerated state. The particles appear to have a fluffy, porous structure with a variety of sizes and shapes. This morphology is typical of as-synthesized iron NPs prior to any thermal treatment **[7]**.

After calcination

The SEM image after calcination shows a significant change in the morphology of the iron NPs. The particles appear to be more defined, with a more uniform and compact structure. The agglomeration and porosity observed in the pre-calcined sample have been reduced, indicating that the calcination process has led to the restructuring and densification of the iron NPs. The elimination of organic matter, the thermal breakdown of remaining components, and the reorganizationof iron structure **[8]**.

V.1.4. Visible ultraviolet absorption spectroscopie visible (UV)

The analysis was done by UV- spectroscopy of Iron oxide nanoparticles before and after calcination using a device (SP-UV 300SRB SPECTROPHOTOMETER) Type of (Spectrum Instruments) and scanning along the wavelength of 200-800 nm.

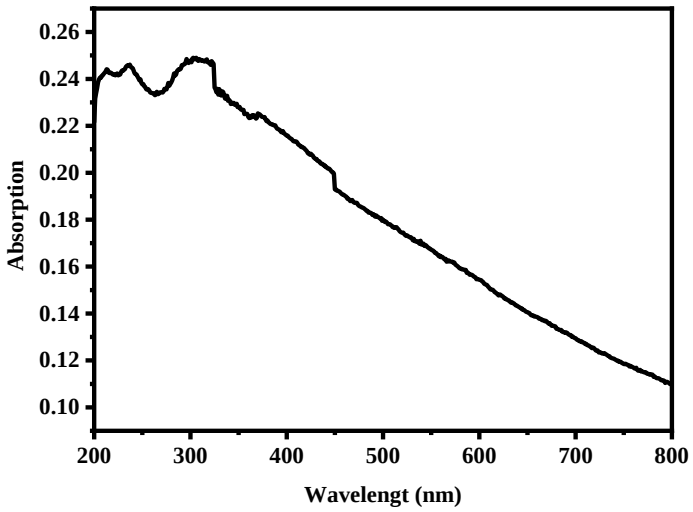


Figure V.4: Spectrum of ultraviolet radiation iron NPs after calcination**.**

Spectrum iron NPs after calcination

There is a maximum absorption peak at 303 nm, which is located in the range (200-400) which crosses the iron oxide nano-bonds Fe_2O_3 **[9]**.

V.1.5. Optical properties

The energy gap Eg can be found from the well known relation: Tauc's relation (Figure V.5) as follows **[10]**: $(ahv)^2 = B(hv - Eg)$……**(*)**

where

B: is a constant.

(hν): is the photon energy.

Eg: is the band gap energy of the sample.

The following results were obtained using three different solvents (distilled water, acetone and acid acetic) Sing by taking 5ml of solvent and adding 1mg of NPs powder after calcination and then placing it in the ultra-son apparatus for agitation **[11,12]**.

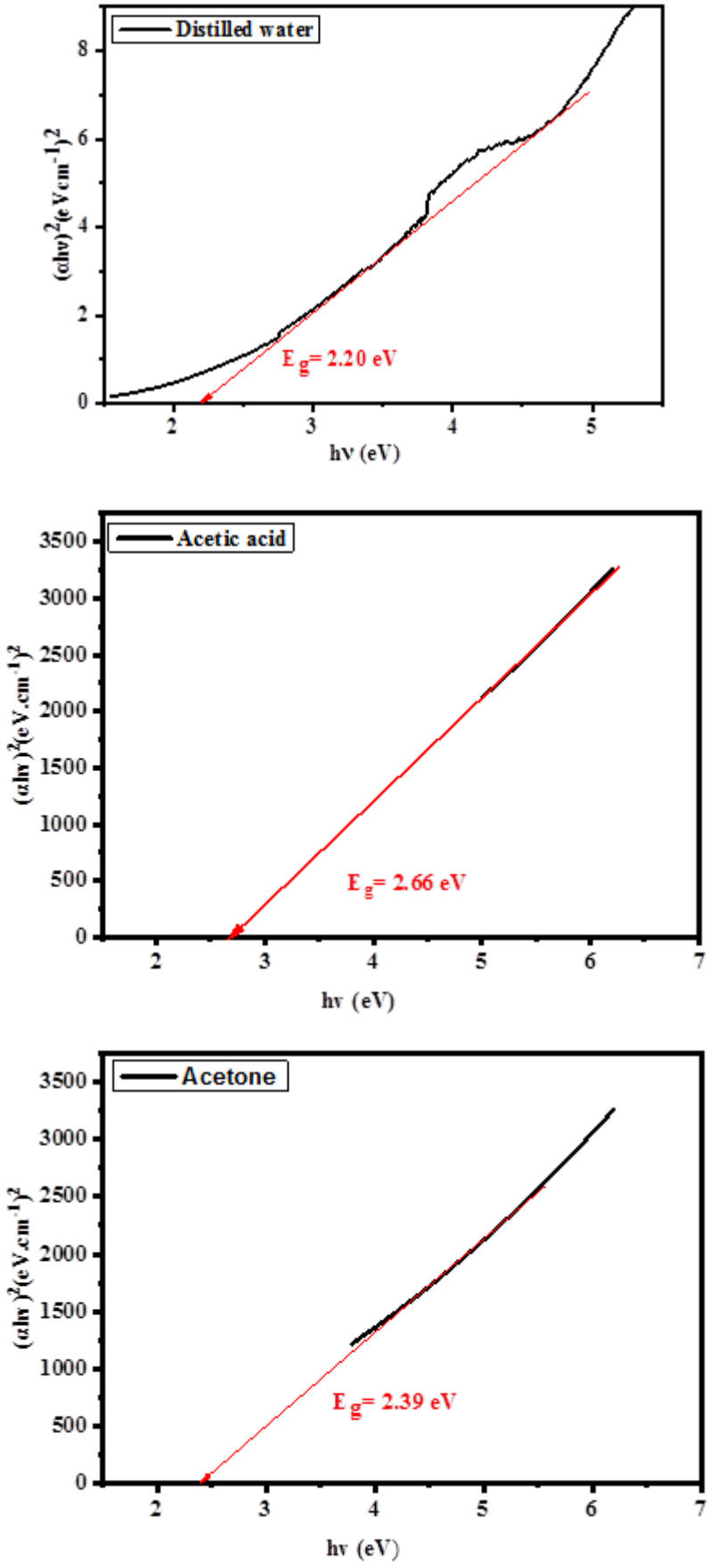


Figure V.5: Band gaps (Eg) estimation from Talc's relation for iron oxide NPs powders for three solvents.

Band gaps energy for NPs were found to be (2.2, 2.66 and 2.39 eV) in distilled water, acetone and acetic acid, respectively. The results were very similar for the three solvents and these values align with a wide range of earlier studies on iron oxide nanoparticles.

V.1.6. pH at point zero charge (pH_{pzc})

The pH was measured at the point of zero charge pH_{pzc} for iron oxide nanoparticles the results are shown in **Figure 6**.

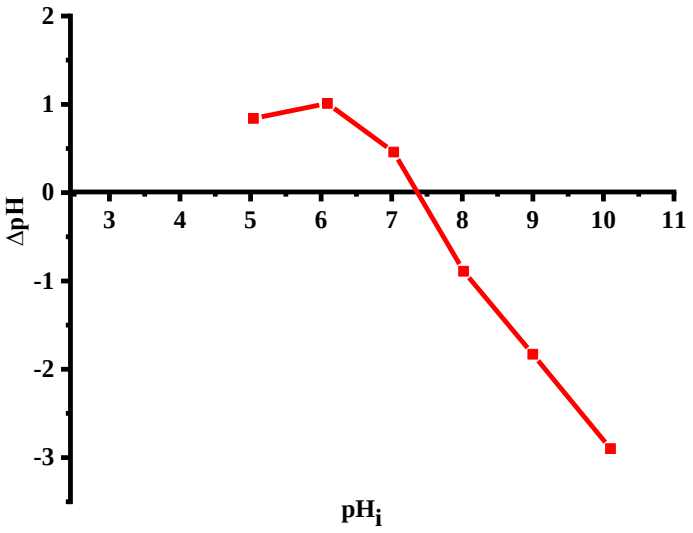


Figure V.6: pH curve at point zero charge (pH_{pzc}).

The figure shows a graph showing the relationship between pH and point zero charge (pH_{pzc}) of iron oxide nanoparticles, zero point charge information can be used to understand the properties of iron oxide nanoparticles, such as their stability and interaction with other molecules.

In the figure it can be seen that the zero point of charge for iron oxide nanoparticles is about 7.4 this means that at a pH below 7.4 the surface of the particles is positively charged and the adsorption of anions is favored At pH higher than 7.4 the surface of the particles is negatively charged which favors the adsorption of cations. In this regard, it is expected that the adsorption of cationic MB by iron oxide nanoparticles is suitable at the pH of the solution higher than 7.4 due to electrostatic interactions **[13]**.

V.2. Choice of pollutant

Four different dyes (methylene blue, methyl orange, Congo red, and crystal violet) were tested for three hours to see how iron oxide nanoparticles affected the removal yield of each dye. mass of nanoparticles 25mg volume of dye solution 25ml. Initial concentration of dye solution is 25mg mg/L. At pH 6.7 and vibration speed 120 rpm.

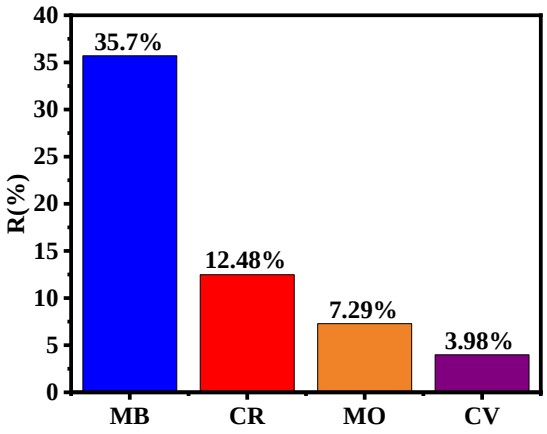


Figure V.7: Adsorption yield of the four dyes on iron NPs.

The adsorption yield of iron oxide nanoparticles on four distinct dyes is depicted in the **Figure V.7**. Methylene blue had the highest yield, at 35.7%, followed by CR and MO, with CV having the lowest yield. Therefore, MB was chosen as the pollutant (adsorbent material) for the remainder of the study.

V.3. Phtocatalysis process

V.3.1. Photocatalytic experiments of MB on iron NPs in different surrounding conditions

The effect of iron oxide nanoparticles on the removal yield of methylene blue (MB) was studied under different ambient conditions (darkness, sunlight, and UV rays) in the time range from 30 to 350 minutes by placing 5 mg of NPs in a 5 ml (MB) solution volume, dye solution concentration (MB) 10 mg/L, and this is done while keeping the remaining values of the variables at the average value.

V.3.1.1. In dark ambient conditions

This curve provides valuable information on the kinetics of methylene blue removal using iron oxide nanoparticles under dark conditions.

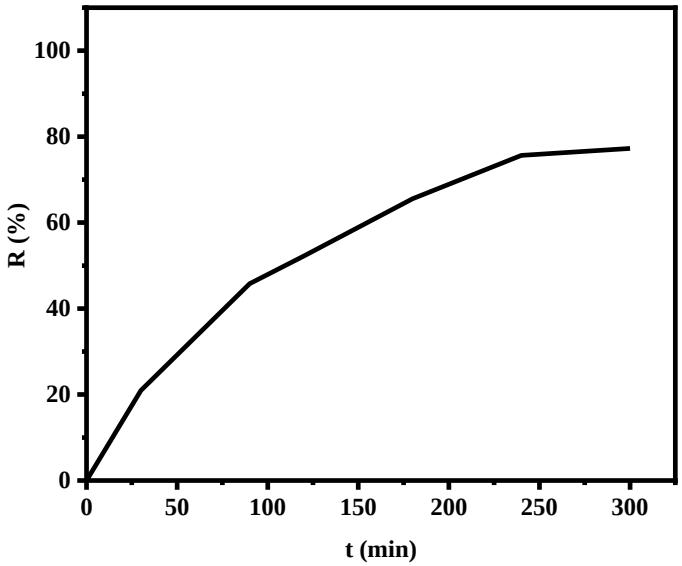


Figure V.8: Removal of MB using iron NPs in dark ambient conditions.

It was observed from **Figure V.8** that the removal rate gradually increases with increasing time, indicating that adsorption on iron oxide nanoparticles becomes more effective with increasing contact duration. In the initial stages (30-90 minutes), the removal rate is faster, which indicates efficient methylene blue adsorption in this period due to the availability of many empty adsorption sites on the surface of the iron oxide nanoparticles,. After that, it continues The removal rate is increasing but at a slower pace, which indicates that the adsorption process is approaching equilibrium due to saturation of the available adsorption sites.

V.3.1.2. Under sunlight

This curve shows the dynamics of the photocatalytic removal of dye using iron oxide nanoparticles in a light-exposed environment.

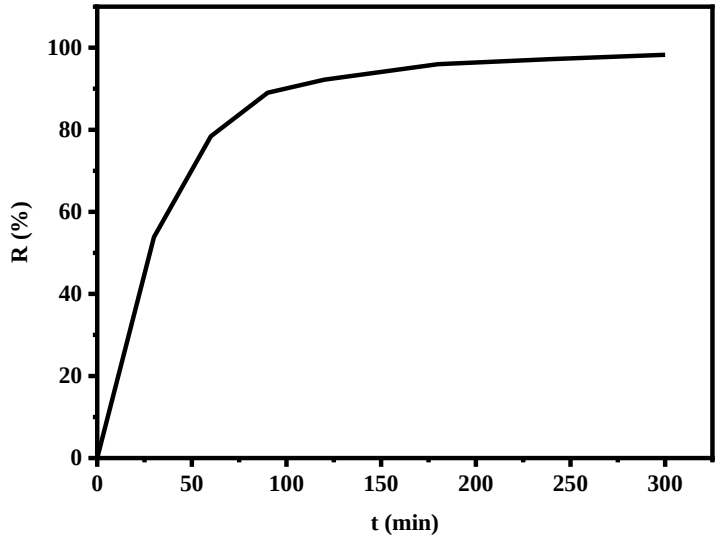


Figure V.9: Removal of MB using iron NPs in sunlight.

The **Figure V.9** shows removal of MB using iron NPs in sunlight. The rate of dye removal increases significantly over time. This reflects the increase in the efficiency of the photocatalytic process, where iron oxide nanoparticles use light energy to stimulate the disassembly and effective removal of the dye. Iron oxide nanoparticles act as a photocatalyst, absorbing light energy and activating the process of producing active oxygen and hydroxyl radicals, which interact with the dye to stimulate its decomposition and removal from the medium.

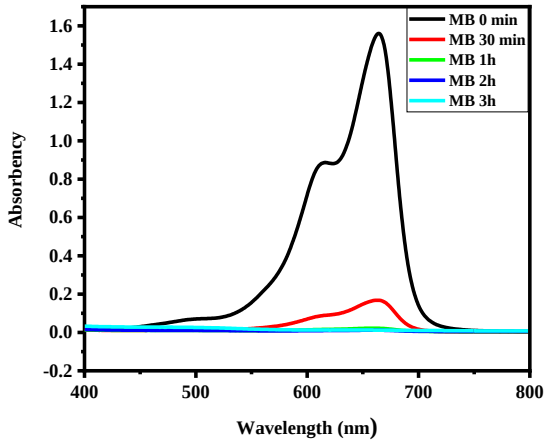


Figure V.10: A visual picture of MB before and after Adsorption of MB dye using iron NPs for 3h.

The UV-visible absorption spectra in **Figure V.10** show the adsorption of methylene blue on iron oxide nanoparticles and how the adsorption process evolves with time. A clear peak appeared around 664 nm, which is the characteristic absorption peak of methylene blue. With

increasing time from 30 minutes to 3 hours., the peak intensity decreases significantly. indicating that adsorption on iron oxide nanoparticles becomes more effective with increasing contact duration due to the decrease in the concentration of methylene blue in the solution and thus the decrease of the peak in the absorption spectrum.

V.3.1.3. In presence of UV:

This curve shows the dynamic of the photocatalytic removal of dye using iron oxide nanoparticles under UV light.

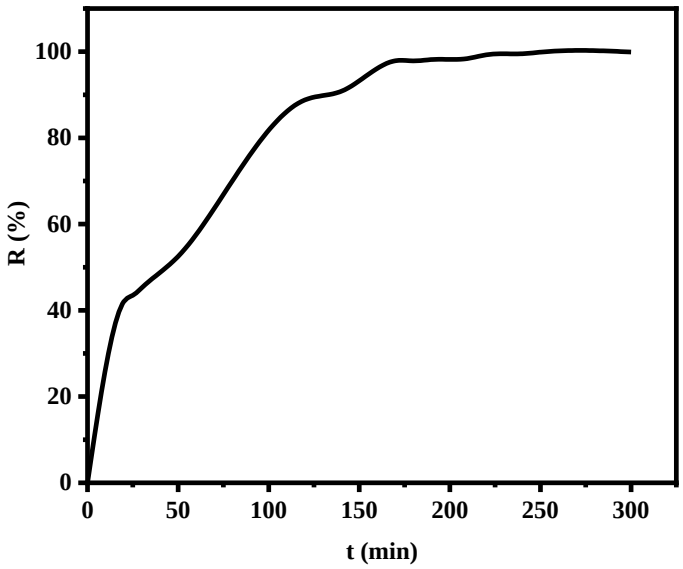


Figure V.11: Removal of MB using iron NPs under UV light.

The **Figure V.11** shows the yield curve of MB removal using iron NPs under UV light. At first, the removal rate is slow reflecting the initial stage of the interaction between nanoparticles and dye. Over time the removal rate begins to increase significantly indicating an increased process efficiency for photocatalysts under the influence of ultraviolet radiation, in the later stages the removal rate begins to stabilize, this may indicate that an equilibrium has been reached due to the saturation of the available absorption sites.

From the analysis of the three curves, it can be concluded that the best conditions for the process of removing methylene blue dye using iron nanoparticles are the presence of ultraviolet radiation to stimulate the photocatalytic process and increase the removal rate. Increasing the contact time also achieves the highest rate of dye absorption on iron nanoparticles.

V.3.2. Adsorption kinetics analysis

- **Adsorption equilibrium in preferential MB adsorption**

In all adsorption experiments, the steady state is reached within 300 min, as shown in Figure V.12 this indicates the fast adsorption kinetics of MB on all NPs surfaces.

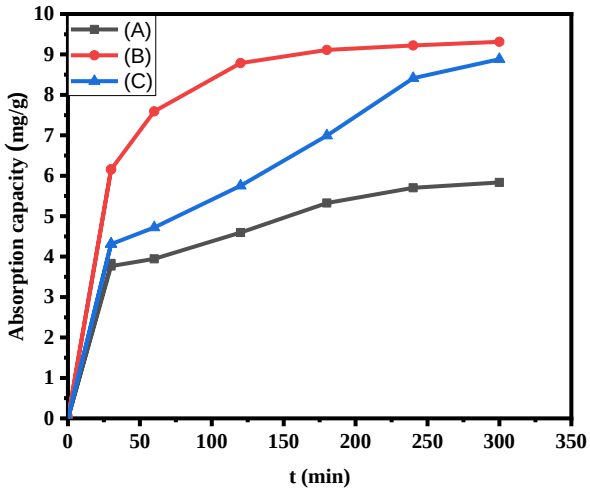


Figure V.12: MB removal capacity using iron NPs under ambient conditions, where (A) in dark ambient conditions, (B) in sunlight, and (C) under UV light

The graph indicates that the absorption capacity of MB dye by iron NPs is significantly affected by environmental conditions. Sunlight enhances the absorption capacity the most, followed by ultraviolet light, while ambient conditions in the dark lead to the lowest absorption. This indicates that light, especially sunlight, plays a crucial role in improving the effectiveness of iron NPs in removing MB dye from solutions.

Pseudo-first-order and pseudo-second-order kinetics of preferential MB adsorption

The results of the analysis of pseudo- second -order kinetics for adsorption of MB particles on NPs surfaces (Table V.1 and Figure V.14) indicate good linearity and good fit of the experimental data for this model compared to the pseudo first-order model which indicated poor linearity and poor fit of the experimental data (Table V.1 and Figure V.13).The q_e (equilibrium absorption amplitude) calculated from the pseudo- second -order kinetic plots is also in very close agreement with the empirical q_e in contrast to the q_e calculated from the pseudo- first -order plots (see Table V.1). This indicates the best compliance of MB adsorption on all surfaces of the iron oxide NPs with pseudo-second-order kinetics.

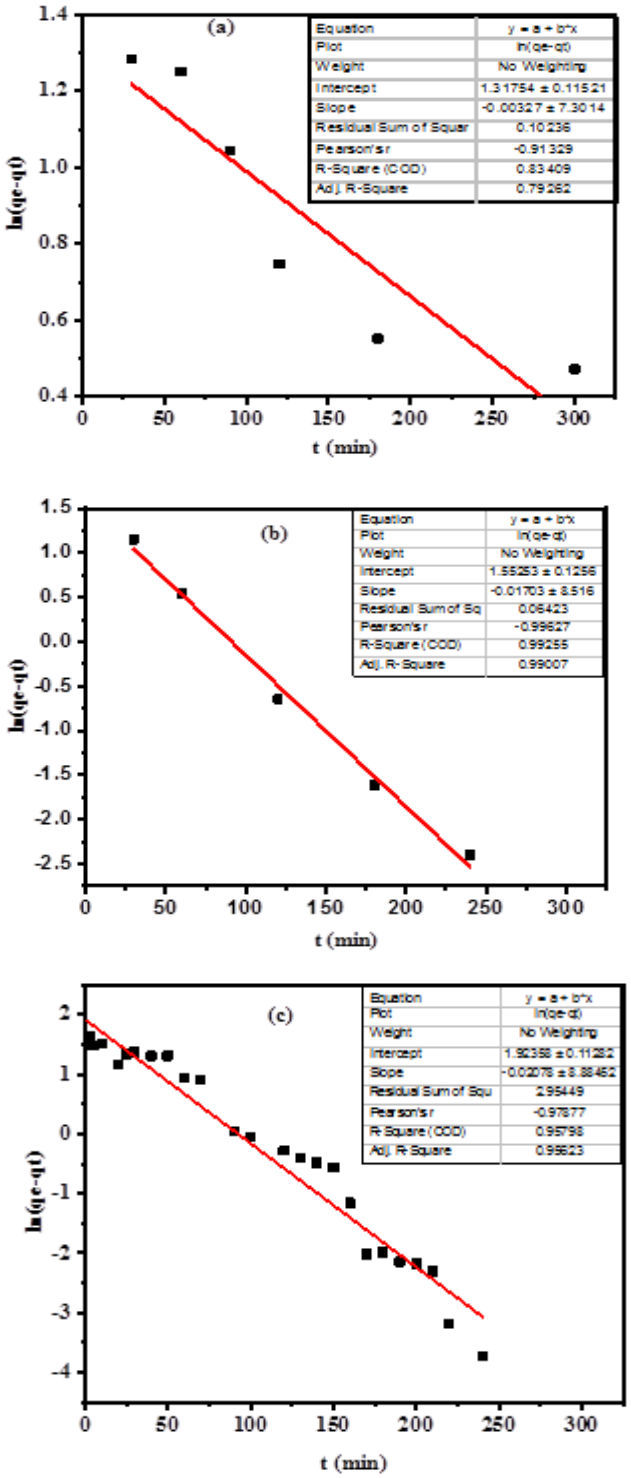


Figure V.13: Plots of the kinetics of the first process for preferential MB adsorption at ambient conditions where (a) in the presence of darkness, (b) in the presence of sunlight, and (c) in the presence of UV radiation.

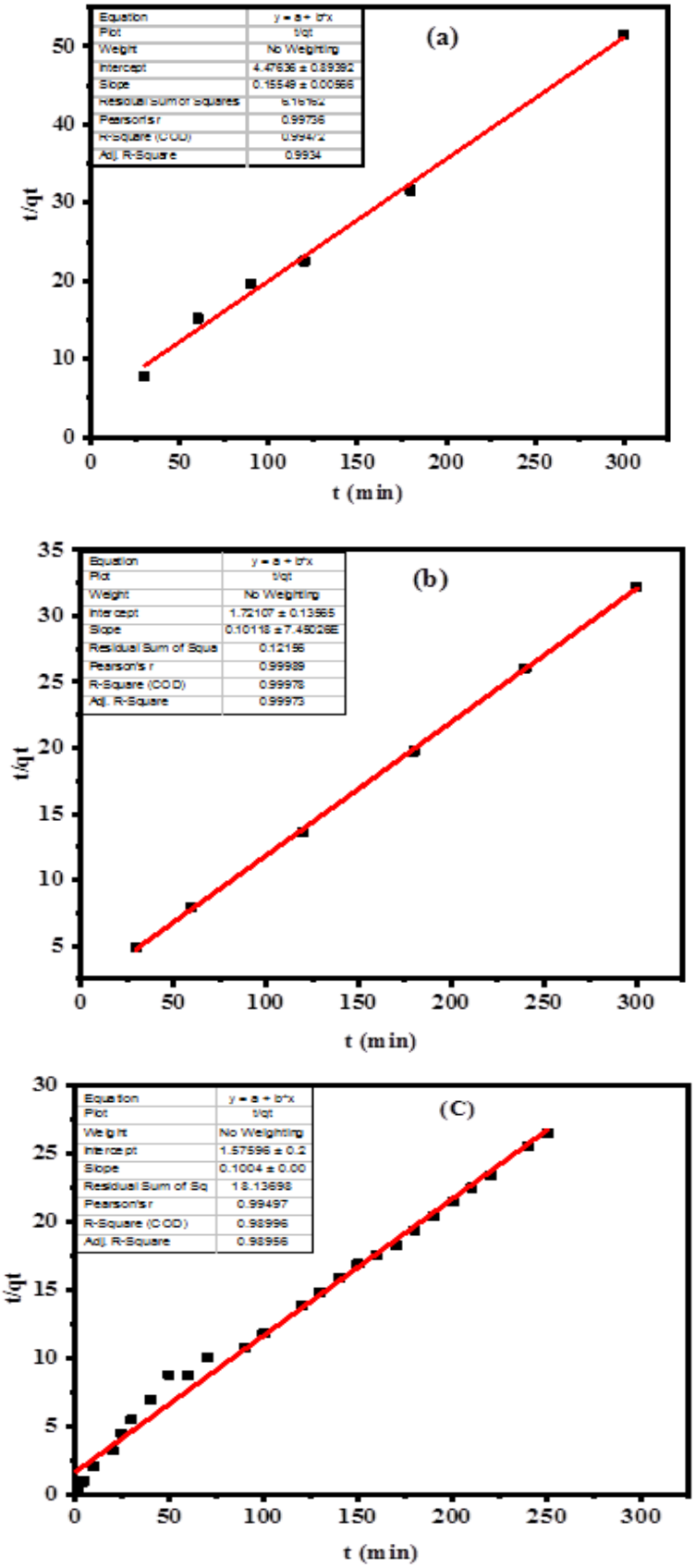


Figure V.14: plots of pseudo-second order kinetics of preferential MB adsorption at ambient conditions where (a) is in the presence of darkness, (b) is in the presence of sunlight and (c) is in the presence of UV.

Table V.1: Adsorption kinetic parameters of MB adsorption on the iron oxide NPs samples in ambient conditions.

Ambient conditions	Concentration (mg/ L)	q_{max} (mg/g)	first order-Pseudo			second order-Pseudo		
			q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (min^{-1})	R^2
Darkness	**10**	**7.4385**	**5.2389**	**0.0037**	**0.8340**	**4.8723**	**0.0040**	**0.9947**
Sunlight	**10**	**9.3118**	**8.3637**	**0.017**	**0.9925**	**8.3637**	**0.0067**	**0.9997**
UV	**10**	**9.4525**	**7.5073**	**0.0207**	**0.9541**	**7.5073**	**0.0073**	**0.9899**

- **Intraparticle diffusion kinetics of preferential MB adsorption in ambient conditions**

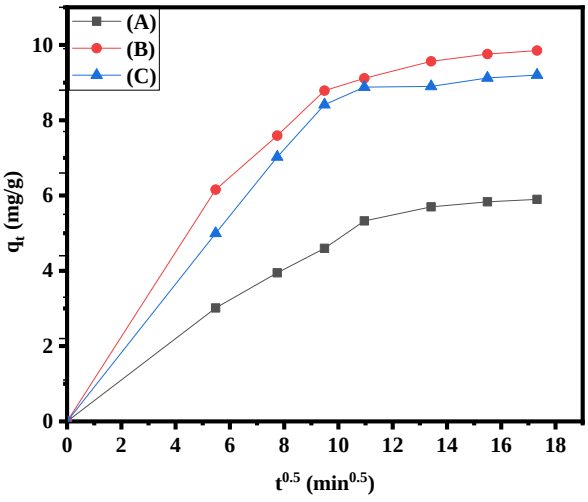


Figure V.15: Representation of the intraparticle diffusion model and adsorption of methylene blue at different ambient conditions.

Table V.2: Intraparticle diffusion model constants R^2 values at different ambient conditions.

Ambient conditions	Concentration (mg/ L)	Constants of the intraparticle diffusion model K_{dif}	R^2
Darkness	**10**	**0.9012**	**0.9038**
Sunlight	**10**	**2.7395**	**0.97995**
UV	**10**	**2.87704**	**0.82888**

We notice in (**Table V.2:** and **Figure V.15:**) the presence of three sections, which indicates that there is a blue adsorption process. MB on the coating of iron NPs was carried out in three stages: external diffusion, gradual adsorption and final equilibrium. Through this study, we observe in the first stage (external diffusion), where methylene blue spread from the solution to the outer surface of the coating, and in the second stage (gradual adsorption), which is a stage in which the rate of adsorption increases relatively, meaning the transfer of methylene blue from the outer surface to the active sites, and in The final stage (final equilibrium) is a stage in which the rate of adsorption equals the rate of diffusion, that is, a decrease in the active sites, the constants of the diffusion model inside the particles, and in the last stage (final equilibrium), which is a stage in which the rate of adsorption is equal With the diffusion rate the active sites free of methylene blue decrease.

V.3.3. FTIR spectroscopy

Infrared spectra help in studying surface interactions and adsorption bonds between nanoparticles and methylene blue molecules, and the following figure shows the infrared spectrum obtained.

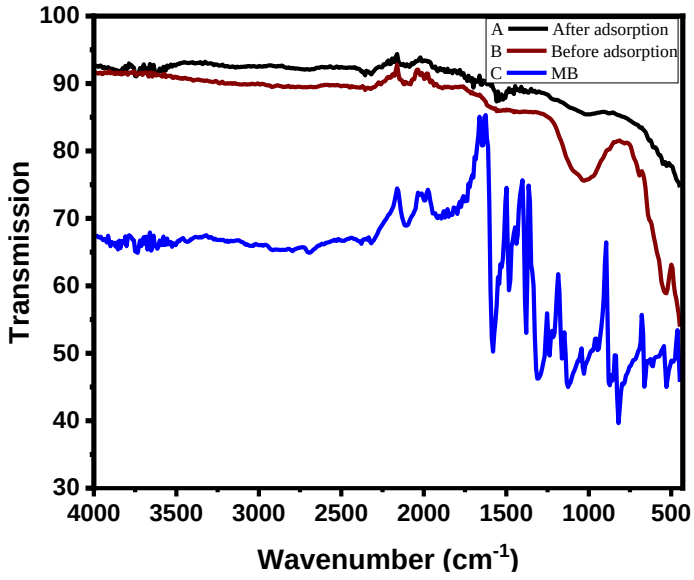


Figure V.16: FTIR spectrum of iron NPs (A) after and (B) before Adsorption, (C) MB.

The FTIR spectrum in **Figure V.16** illustrates variations between different samples of iron oxide nanoparticles before and after methylene blue dye adsorption. Curve (C) represents the spectrum of free methylene blue, which can be compared to the new bands in curve (A) to confirm the adsorption of the dye onto the nanoparticles .Prior to adsorption, depicted in Figure (B), distinctive absorption bands corresponding to Fe-O bonds within the (400-500) range are evident. Conversely, in the post-MB adsorption infrared spectrum, new absorption bands emerge at 1600, 1394.3, and 1336.21 cm, suggesting the presence of N-H, C=N, and C-N bonds characteristic of the methylene blue molecule attached to the particle surface. **[14]**.Based on these observations, it can be concluded that iron oxide nanoparticles successfully adsorbed methylene blue molecules, resulting in noticeable changes in the infrared spectrum **[15]**.

V.3.4. X-ray diffraction (XRD)

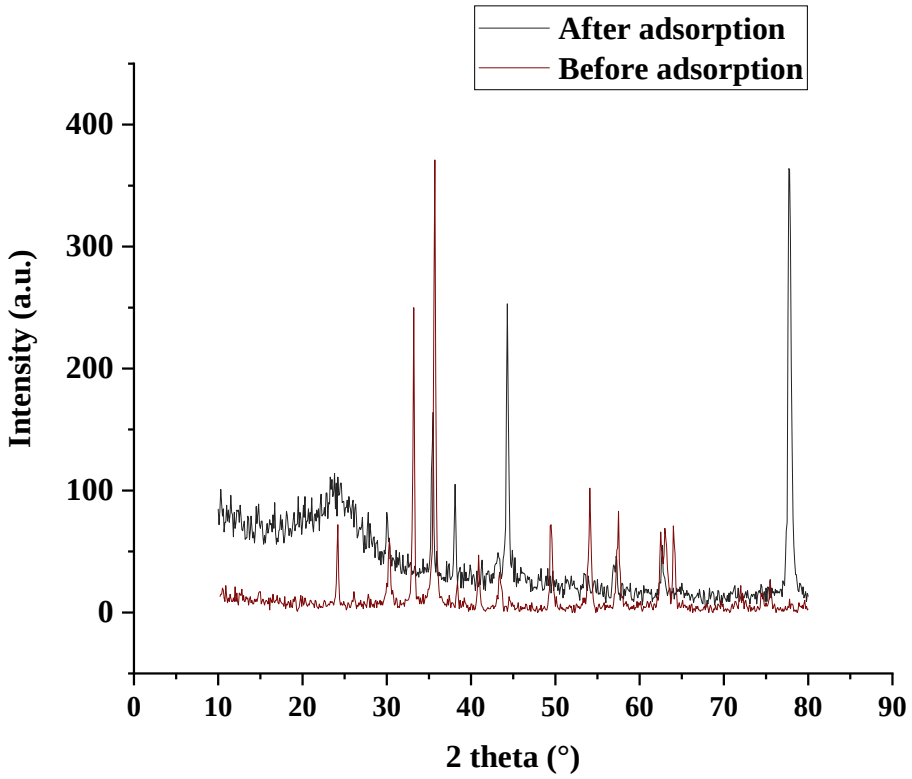


Figure V.17: The provided XRD pattern shows the diffraction data for the magnetic iron nanoparticles (NPs) before and after the adsorption of methylene blue.

Here's a detailed explanation based on the XRD patterns:

1. **Before Adsorption**:

- The XRD pattern shows distinct peaks, indicating the crystalline nature of the nanoparticles.
- The peaks can be associated with the characteristic planes of the iron oxide phases, such as Fe_3O_4 (magnetite) or γ-Fe_2O_3 (maghemite).

2. After Adsorption:

- The XRD pattern remains largely similar to the one before adsorption, with no significant shifts in peak positions.
- This suggests that the adsorption of methylene blue does not alter the crystal structure of the iron oxide nanoparticles.
- There is, however, a slight change in the intensity of some peaks, which might be attributed to surface interactions between the methylene blue molecules and the nanoparticles.

Specific Analysis

- **Peak Identification**: The primary peaks in both patterns can be matched against standard diffraction patterns of iron oxides to confirm the phases present.
- **Intensity Changes**: The slight changes in peak intensity post-adsorption might indicate surface modifications or slight changes in the crystallite size or strain due to the adsorption process.

Detailed Peak Analysis

- **Before Adsorption**: Peaks around 2θ = 30°, 35°, 43°, 57°, and 63° can be associated with the (220), (311), (400), (511), and (440) planes of Fe_3O_4, respectively.
- **After Adsorption**: The same peaks are present, indicating that the crystal structure of Fe_3O_4 is maintained. The relative intensities of these peaks might vary slightly due to the presence of methylene blue on the surface of the nanoparticles.

During methylene blue adsorption, the nanoparticles maintain their crystalline structure, with peaks at similar 2θ values, indicating that the adsorption process does not compromise the structural integrity of the nanoparticles. However, slight changes in peak intensities suggest surface interactions with methylene blue molecules. After adsorption and subsequent regeneration via thermal treatment at 150°C, the XRD pattern shows sharper peaks, particularly at 2θ = 30°, 35°, 43°, 57°, and 63°, indicating effective removal of methylene blue and enhanced crystallinity **[16]**.

V.4. Mathematical modeling of water treatment

This table shows the independent variables of the mathematical modeling experiment for water treatment. These variables help determine the optimal conditions for the water treatment

process to achieve the best results by controlling the amount of additive, reaction duration, and pH.

Table V.3: Values of independent variables excluded in mathematical modeling.

Independent variables	**m (mg/g)**	**t (min)**	**pH**
Interval	25 – 100	30 – 120	4 – 10

V.4.1. Absorbance study

V.4.1.1. Statistical analysis

Table V.4: Table Analysis of variance (ANOVA) for MB absorption

Source	Sum of Squares	d_f	Mean Square	F-value	p-value	
Model	2.35	9	0.2611	62.12	< 0.0001	Significant
A-m	0.1012	1	0.1012	24.09	0.0017	
B-t	1.56	1	1.56	370.55	< 0.0001	
C-pH	0.0325	1	0.0325	7.73	0.0273	
AB	0.0462	1	0.0462	11.00	0.0128	
AC	0.0182	1	0.0182	4.34	0.0758	
BC	0.0025	1	0.0025	0.5947	0.4658	
A^2	0.0400	1	0.0400	9.52	0.0177	
B^2	0.5012	1	0.5012	119.22	< 0.0001	
C^2	0.0178	1	0.0178	4.23	0.0787	
Residual	0.0294	7	0.0042			
Lack of Fit	0.0294	3	0.0098			
Pure Error	0.0000	4	0.0000			
Cor Total	2.38	16				

The model F-value of 62.12 implies the model is significant. This implies that the overall model is statistically significant it can also Inferring the acceptance of the mathematical model by considering the probability value, P-Value, which is less than 0.0001.

As stated in the table. Through the criteria of variance (ANOVA), the mathematical model is considered acceptable if the probability value was less than 0.0500.

Through the table ‹The P value less than 0.0500 indicate significant model terms. Specifically, in this instance, terms A, B, C, AB, A^2, and B^2 are deemed significant. Conversely, values surpassing 0.1000 suggest insignificance in model terms. If numerous

model terms are found to be insignificant (excluding those essential for maintaining hierarchy), reducing the model may enhance its efficacy.

V.4.1.2. Fit Statistics

Std. Dev.	**0.0648**	**R^2**	**0.9876**
Mean	**0.6388**	**Adjusted R^2**	**0.9717**
C.V. %	**10.15**	**Predicted R^2**	**0.8021**
		Adeq Precision	**23.6043**

From the table we note that the value of the regression coefficient for the model R^2=0.9876 Very close to 1which It indicates the acceptability of the mathematical model.

As we note the predicted R^2 of 0.8021 agrees reasonably well with the adjusted R^2 of 0.9717 That is, the difference is less than 0.2, which indicates the strength of the mathematical model in predicting the results.

The Adeq Precision value measures the signal-to-noise ratio. It is recommended that the ratio be greater than 4. The resulting value of 23.604 indicates a very good and sufficient signal, enabling this model to be used to navigate in the design space.

V.4.1.3. Mathematical equation

As per the experimental design software,, the measured experimental absorption (A) was linked and the independent variables in the mathematical equation as follows:

V.4.1.4. The final equation in terms of the Actual Factors of the independent variables

$$A=+2.26409-0.011480*m-0.061123*t-0.030694*pH+0.000115*m\ t-0.000600*m\ pH-0.000333*t\ pH + 0.000069*m^2 + 0.000552*t^2 + 0.007222*pH^2$$

The equation can be used in terms of actual factors to calculate the actual value of adsorption by replacing the independent variables with their actual values. . Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

V.4.2. Diagnosis

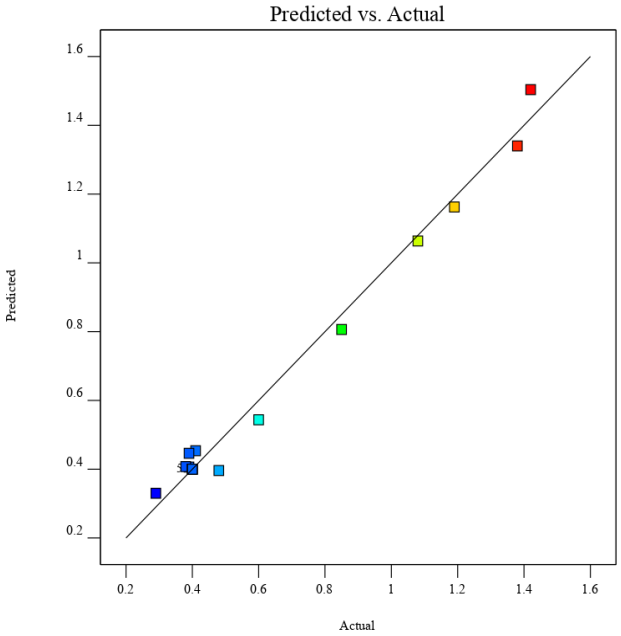


Figure V.18: Curve of predicted and experimental values of adsorption (A)**.**

The figure shows the positioning of the experimental and expected values of absorbance (A) with respect to the first bisector using the mathematical model for the adsorption of methylene blue dye on iron oxide nanoparticles. The graph shows a good linear relationship between the expected values and the actual values of adsorption, which indicates the strength and ability of the model in prediction through its ability to effectively capture the adsorption behavior.

V.4.2.1.The change in the amount of absorbance as a function of mass and adsorption time

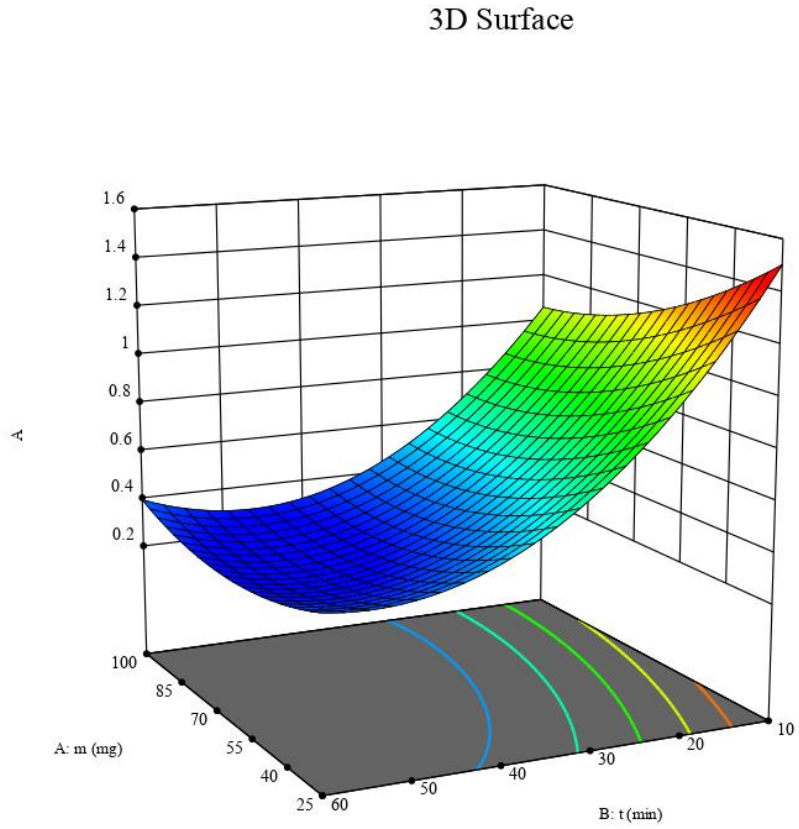


Figure V.19: Absorption change curve as a function of mass and adsorption time.

The figure represents a three-dimensional surface plot of the variation of absorption removal of methylene blue as a function of mass and time. Adsorbance is lower in the blue areas of the plot at low masses and shorter contact times, and reaches its highest values in the red/orange areas of the plot with increasing mass and time, where absorption increases from 0.2 to 1.4 due to the effect of mass and time together. However, change in mass appears to have a greater effect on the range of absorbance values than change in time a change in mass from about 20 to 85 mg results in a significant change in absorbance values, while a change in time from about 10 to 60 minutes results in a noticeable change in absorbance values, but less than the mass.

V.4.3. Yield study

V.4.3.1. Statistical analysis

Table V.5: Analysis of Variance (ANOVA) for MB removal yield.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6662.97	9	740.33	62.12	< 0.0001	significant
A-m	287.08	1	287.08	24.09	0.0017	
B-t	4416.40	1	4416.40	370.55	< 0.0001	
C-pH	92.18	1	92.18	7.73	0.0273	
AB	131.06	1	131.06	11.00	0.0128	
AC	51.67	1	51.67	4.34	0.0758	
BC	7.09	1	7.09	0.5947	0.4658	
A^2	113.49	1	113.49	9.52	0.0177	
B^2	1420.97	1	1420.97	119.22	< 0.0001	
C^2	50.44	1	50.44	4.23	0.0787	
Residual	83.43	7	11.92			
Lack of Fit	83.43	3	27.81			
Pure Error	0.0000	4	0.0000			
Cor Total	6746.40	16				

The model F-value of 62.12 implies the model is significant. This implies that the overall model is statistically significant it can also Inferring the acceptance of the mathematical model by considering the probability value, P-Value, which is less than 0.0001.

As stated in the table. Through the criteria of variance (ANOVA), the mathematical model is considered acceptable if the probability value was less than 0.0500.

Through the table ‹The P value less than 0.0500 indicate significant model terms. Specifically, in this instance, terms A, B, C, AB, A^2, and B^2 are deemed significant. Conversely, values surpassing 0.1000 suggest insignificance in model terms. If numerous model terms are found to be insignificant (excluding those essential for maintaining hierarchy), reducing the model may enhance its efficacy.

V.4.3.2. Fit Statistics

Std. Dev.	3.45	R^2	0.9876
Mean	65.98	Adjusted R^2	0.9717
C.V. %	5.23	Predicted R^2	0.8021
		Adeq Precision	23.6043

The Predicted R^2 of 0.8021 is in reasonable agreement with the Adjusted R^2 of 0.9717. The difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.604 indicates an adequate signal. This model can be used to navigate the design space.

V.4.3.3. Mathematical equation:

As per the experimental design software, the measured experimental yield (R %) was linked and the independent variables in the mathematical equation as follows:

V.4.3.4. The final equation in terms of the Actual Factors of the independent variables

$$R = -20.55851 + 0.611289 * m + 3.25470 * t + 1.63442 * pH - 0.006106 * m\,t + 0.031949 * m\,pH + 0.017749 * t\,pH - 0.003692 * m^2 - 0.029393 * t^2 - 0.384570 * pH^2$$

The equation can be used in terms of actual factors to calculate the actual value of the return by replacing the independent variables with their actual values. This equation cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate units of each.

V.4.4. Diagnosis

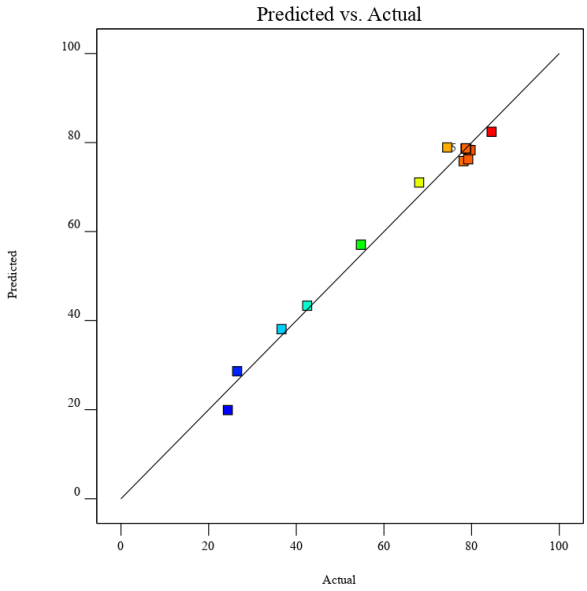


Figure V.20: Curve of expected and experimental values of yield (R %).

The figure shows the positioning of the experimental and expected values of the yield (R%) in relation to the first bisector by the model Mathematical analysis of adsorption, where the strength and prediction ability of the model are demonstrated by observing the extent of agreement and closeness of the experimental and predicted values.

V.4.5. Change in the amount of yield as a function of pH and adsorption time :

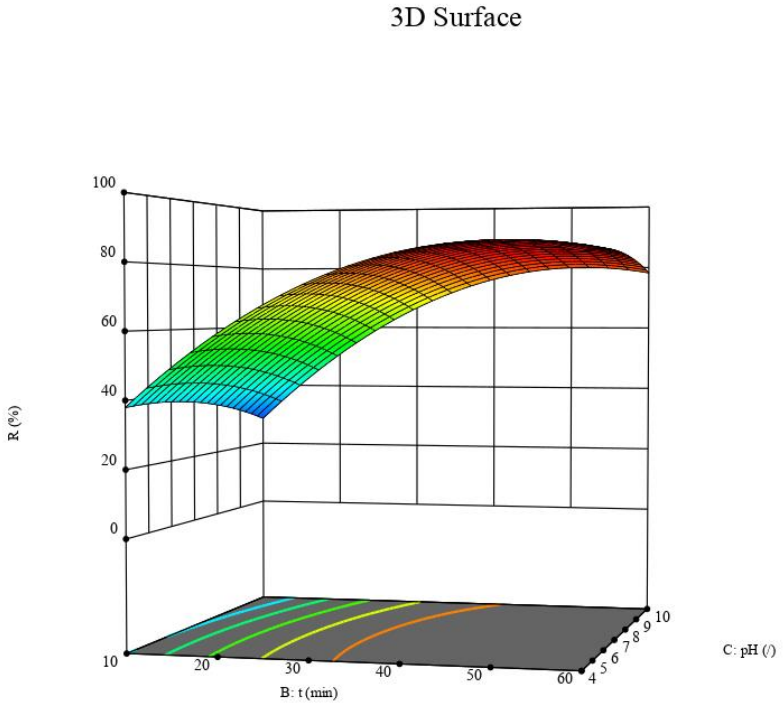


Figure V.21: Yield change curve as a function of time and pH.

The **Figure V.21** represents a three-dimensional plot of the variation of methylene blue removal yield as a function of time and pH، the chart indicates that the dye removal yield is affected by both pH and time. Where the return increases from 24.3876 to 84.558. Changing the pH value has a significant impact on the change in the removal yield. It is observed that the region with high efficiency of 85% is located in the pH range of approximately 6 to 7. Outside of this ideal pH range, the removal efficiency decreases significantly, this is because the NPs are positively charged at pHs in this range attracting negatively charged MB molecules. While the NPs are negatively charged at high pH, which repel the negatively charged MB molecules. Increasing the time has a significant positive effect on increasing the removal yield. Efficiency reaches its highest values at a contact time of 60 minutes or more, but the gradual effect of contact time on efficiency appears less severe compared to the effect of pH.

V.4.6. Capacity study

V.4.6.1. Statistical analysis

Table V.6: Table Analysis of variance (ANOVA) for MB Capacity.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	50.90	9	5.66	53.62	< 0.0001	significant
A-m	26.80	1	26.80	254.07	< 0.0001	
B-t	12.46	1	12.46	118.15	< 0.0001	
C-pH	0.4220	1	0.4220	4.00	0.0856	
AB	5.13	1	5.13	48.62	0.0002	
AC	0.4306	1	0.4306	4.08	0.0831	
BC	0.0106	1	0.0106	0.1005	0.7605	
A^2	3.39	1	3.39	32.15	0.0008	
B^2	2.53	1	2.53	24.03	0.0017	
C^2	0.0196	1	0.0196	0.1856	0.6795	
Residual	0.7383	7	0.1055			
Lack of Fit	0.7383	3	0.2461			
Pure Error	0.0000	4	0.0000			
Cor Total	51.64	16				

The model F-value of 53.62 implies the model is significant. This implies that the overall model is statistically significant it can also Inferring the acceptance of the mathematical model by considering the probability value, P-Value, which is less than 0.0001.

As stated in the table. Through the criteria of variance (ANOVA), the mathematical model is considered acceptable if the probability value was less than 0.0500. Through the table ،The P value less than 0.0500 indicate significant model terms. Specifically, in this instance, terms A, B, C, AB, A^2, and B^2 are deemed significant. Conversely, values surpassing 0.1000 suggest insignificance in model terms. If numerous model terms are found to be insignificant (excluding those essential for maintaining hierarchy), reducing the model may enhance its efficacy.

V.4.6.2. Fit Statistics

Std. Dev.	**0.3248**	R^2	**0.9857**
Mean	2.99	**Adjusted R^2**	0.9673
C.V. %	10.88	**Predicted R^2**	0.7712
		Adeq Precision	26.9199

From the table we note that the value of the regression coefficient for the model R^2=0.9857 Very close to 1which It indicates the acceptability of the mathematical model.

As we note the predicted R^2 of 0.7 712 agrees reasonably well with the adjusted R^2 of 0.9673 That is, the difference is less than 0.2, which indicates the strength of the mathematical model in predicting the results

The Adeq Precision value measures the signal-to-noise ratio. It is recommended that the ratio be greater than four are. The resulting value of 26.920 indicates a very good and sufficient signal, enabling this model to be used to navigate in the design space.

V.4.6.3. Mathematical equation:

As per the experimental design software, the measured experimental Capacity (q) was linked and the independent variables in the mathematical equation as follows:

$$q = +4.20292 \ -0.106720 * m +0.207500 * t -0.176774 * pH -0.001208 * m\ t +0.002916 * m\ pH +0.000686 * t\ pH +0.000638 * m^2 -0.001241 * t^2 -0.007577 * pH^2$$

V.4.6.4. The final equation in terms of the Actual Factors of the independent variables:

The equation can be used in terms of actual factors to calculate the actual value of Capacity by replacing the independent variables with their actual values. . Here, the levels should be specified in the original units for each factor. This equation cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate units of each.

V.4.6.5. Diagnosis

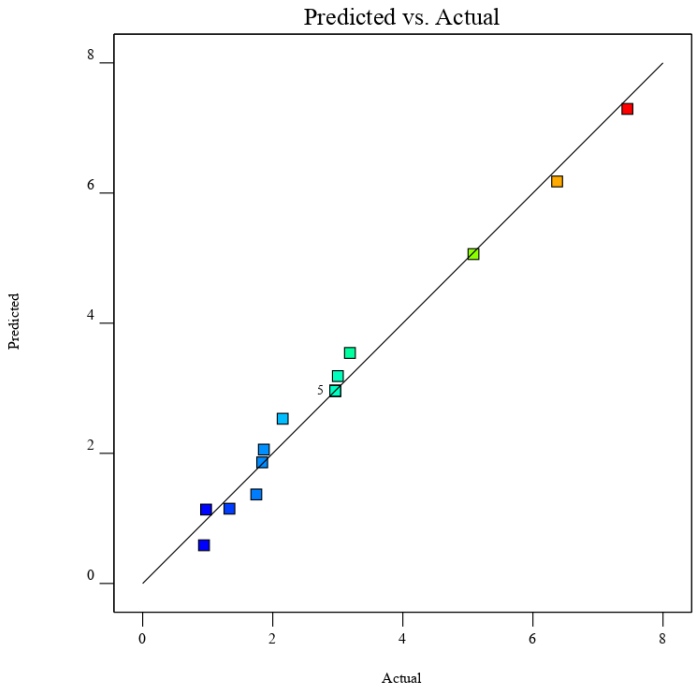


Figure V.22: Curve of expected and experimental values of Capacity (q).

The **Figure V.22** shows the positioning of the experimental and expected values of Capacity (q).With respect to the first bisector using the mathematical model for the adsorption of methylene blue dye on iron oxide nanoparticles. The graph shows a good linear relationship between the expected values and the actual values of adsorption, which indicates the strength and ability of the model in prediction through its ability to effectively capture the adsorption behavior.

V.4.6.6. The change in Capacity as a function of mass and pH

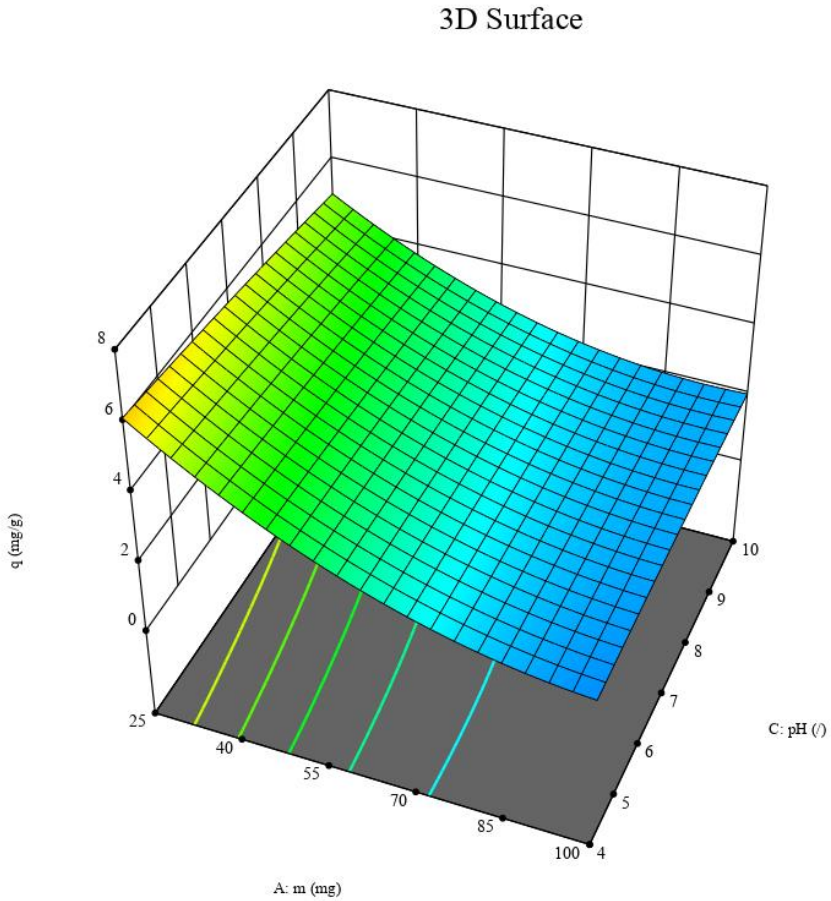


Figure V.23: Capacity change curve as a function of mass and pH.

The **Figure V.23** represents a three-dimensional plot of the variation of methylene blue removal Capacity as a function of mass and pH، the 3D surface curve shows the adsorption capacity of methylene blue dye on iron oxide nanoparticles as a function of mass and pH, the adsorbed Capacity ranges from less 2 to 6 mg/g. It can be seen that the adsorbed capacity gradually increases with the change in mass and pH until it reaches a maximum value before stabilizing or starting to decrease slightly.

The capacity-adsorbed increases with mass and decreases in pH with increasing pH, even if the mass increases, the capacity adsorbed does not increase significantly and may even

decrease. It can be concluded that it is better to work at low pHs while increasing the mass to the point after which no saturation or decrease in the capacity adsorbed occurs.

V.4.7. Table of actual and expected values for

Table V.7: Experimental values and expected values of variables (A, R and q)

Run 1 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.454	0.454	0.410	0.065	0.056
R	75.839	75.839	78.168	3.452	2.990
q	1.862	1.862	1.838	0.325	0.281
Run 2 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.806	0.806	0.850	0.065	0.056
R	57.069	57.069	54.739	3.452	2.990
q	5.063	5.063	5.086	0.325	0.281
Run 3 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.400	0.400	0.400	0.065	0.029
R	78.701	78.701	78.701	3.452	1.544
q	2.961	2.961	2.961	0.325	0.145
Run 4 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.330	0.330	0.290	0.065	0.056
R	82.428	82.428	84.558	3.452	2.990
q	3.543	3.543	3.187	0.325	0.281
Run 5 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.408	0.408	0.380	0.065	0.056
R	78.301	78.301	79.766	3.452	2.990
q	3.187	3.187	3.002	0.325	0.281
Run 6 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	1.340	1.340	1.380	0.065	0.056
R	28.648	28.648	26.518	3.452	2.990

q	0.588	0.588	0.943	0.325	0.281
Run 7 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	1.504	1.504	1.420	0.065	0.056
R	19.928	19.928	24.388	3.452	2.990
q	2.532	2.532	2.153	0.325	0.281
Run 8 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.446	0.446	0.390	0.065	0.056
R	76.238	76.238	79.233	3.452	2.990
q	2.058	2.058	1.863	0.325	0.281
Run 9 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.396	0.396	0.480	0.065	0.056
R	78.900	78.900	74.441	3.452	2.990
q	1.368	1.368	1.748	0.325	0.281
Run 10 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.400	0.400	0.400	0.065	0.029
R	78.701	78.701	78.701	3.452	1.544
q	2.961	2.961	2.961	0.325	0.145
Run 11 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.544	0.544	0.600	0.065	0.056
R	71.046	71.046	68.051	3.452	2.990
q	6.178	6.178	6.373	0.325	0.281
Run 12 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	1.064	1.064	1.080	0.065	0.056
R	43.357	43.357	42.492	3.452	2.990
q	1.137	1.137	0.976	0.325	0.281
Run 13 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**

A	1.163	1.163	1.190	0.065	0.056
R	38.099	38.099	36.635	3.452	2.990
q	1.150	1.150	1.335	0.325	0.281
Run 14 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.400	0.400	0.400	0.065	0.029
R	78.701	78.701	78.701	3.452	1.544
q	2.961	2.961	2.961	0.325	0.145
Run 15 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.406	0.406	0.390	0.065	0.056
R	78.368	78.368	79.233	3.452	2.990
q	7.293	7.293	7.454	0.325	0.281
Run 16 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.400	0.400	0.400	0.065	0.029
R	78.701	78.701	78.701	3.452	1.544
q	2.961	2.961	2.961	0.325	0.145
Run 17 Response	**Predicted Mean**	**Predicted Median**	**Observed**	**Std Dev**	**SE Mean**
A	0.400	0.400	0.400	0.065	0.029
R	78.701	78.701	78.701	3.452	1.544
q	2.961	2.961	2.961	0.325	0.145

V.5. Optimal values of adsorption conditions

From **Figure V.24**, methylene blue was adsorbed with an amount of iron NPs estimated at 74 mg, a diffusion time of 52.9 minutes, at a pH = 7.2, a shaking speed of 450 rpm, where in Under these experimental conditions, the diffusion yield was 86.03%.

These optimum values were validated through repeated confirmatory experiments and yielded results the conditions Optimum have return rates of 90.12 %, 84.25 %, and 76.02 %, with an average yield of 83.67 %, and through the model's prediction of an adsorption yield of 86.03%, we find that:

Absolute error = |predicted value – experimental value|=4.09.

Relative error = ((experimental value + absolute error) - experimental value) / and experimental value= 0.045

That is 4.54 %. This indicates that this mathematical model can be used to improve the experimental conditions for MB adsorption **[17]**.

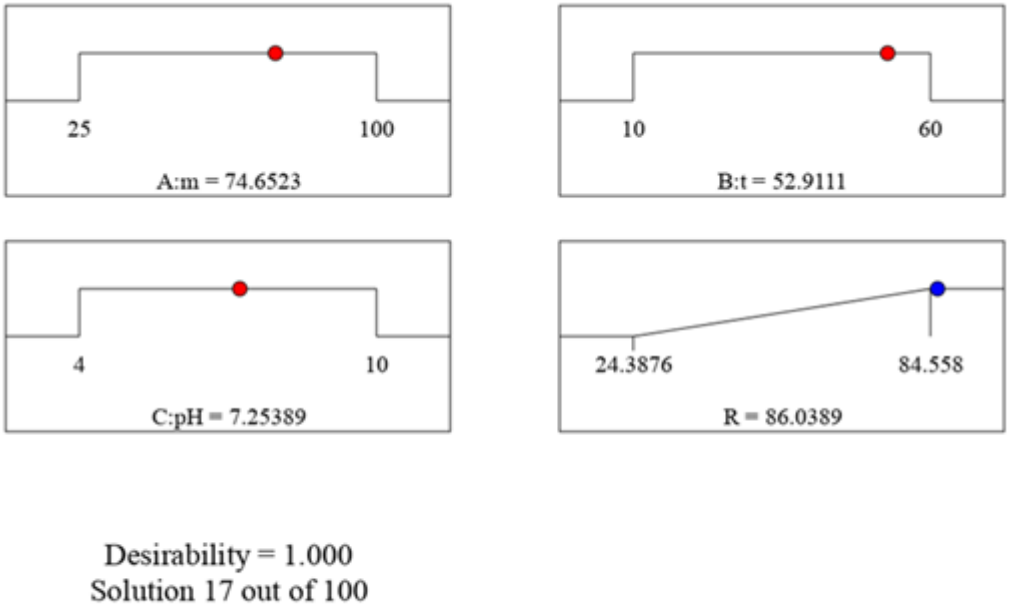


Figure V.24: Optimum value curves for the adsorption process.

V.5.1. Experiment on the recovery and reuse of iron NPs

After the adsorption process, the iron nanoparticles were recovered by centrifugation and dried in a high-temperature environment in preparation for usage in a later cycle.

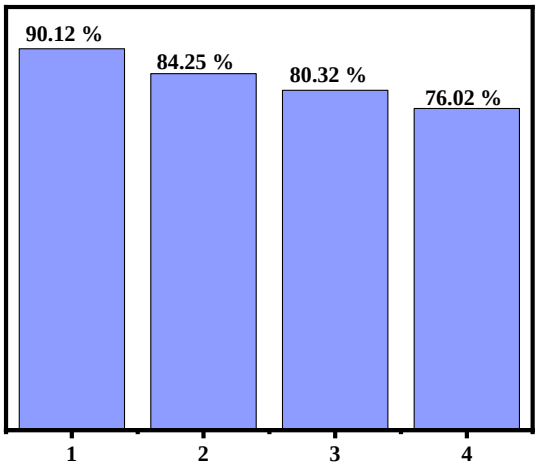


Figure V.25: Adsorption yield of methylene blue over four cycles.

Four MB removal yield cycles on iron NPs are depicted in the **Figure V.22**. The **Figure V.23** illustrates how the first return matches the value that was previously obtained either experimentally or as predicted and whose convergence we have already demonstrated. The adsorbent continues to hold onto some methylene blue dye, which causes the removal yield to start declining after the second cycle to 80.32 %. Which calcination is unable to eliminate. These suspended molecules may be chemically bonded to certain functions on the surface of the iron NPs or they could be imprisoned inside the pore- and gap-filled particles.This experiment shows that iron nanoparticles are reusable, indicating their sustainability**[18]**.

V.5.2. FTIR spectroscopy of iron NPs before and adsorption after calcinations

This spectrum shows the vibrational properties of iron oxide nanoparticles both before to adsorption and after calcination to eliminate the methylene blue dye.

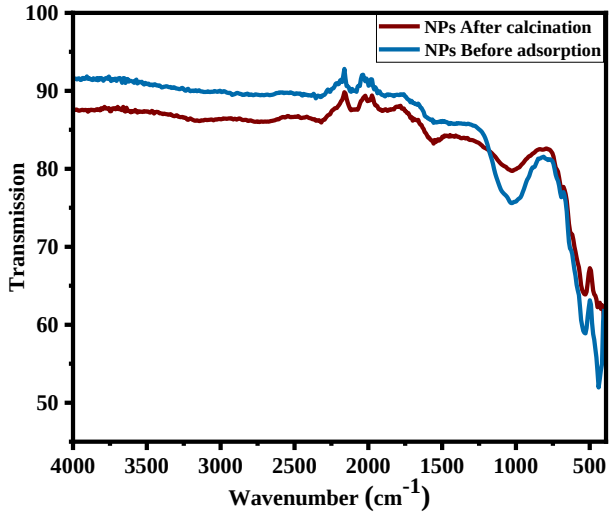


Figure V.26: FTIR spectrum of iron NPs after and before adsorption.

Before adsorption, the Fe–O vibration absorption band is visible in the 400–500 cm^{-1} region. After calcination, it can be noticed that the bands linked to the absorbed organic molecules (N-H, C=N, and C-N, which are linked to the methylene blue dye) are completely disappeared. It seems that both spectra are perfectly similar, with a few minor band variations that might suggest the existence of residues. The two spectra's resemblance verifies the iron oxide nanoparticles sustainability and their potential for reuse when they are subjected to highly temperature atmosphere **[19]**.

V.5.3. X-ray diffraction (XRD)

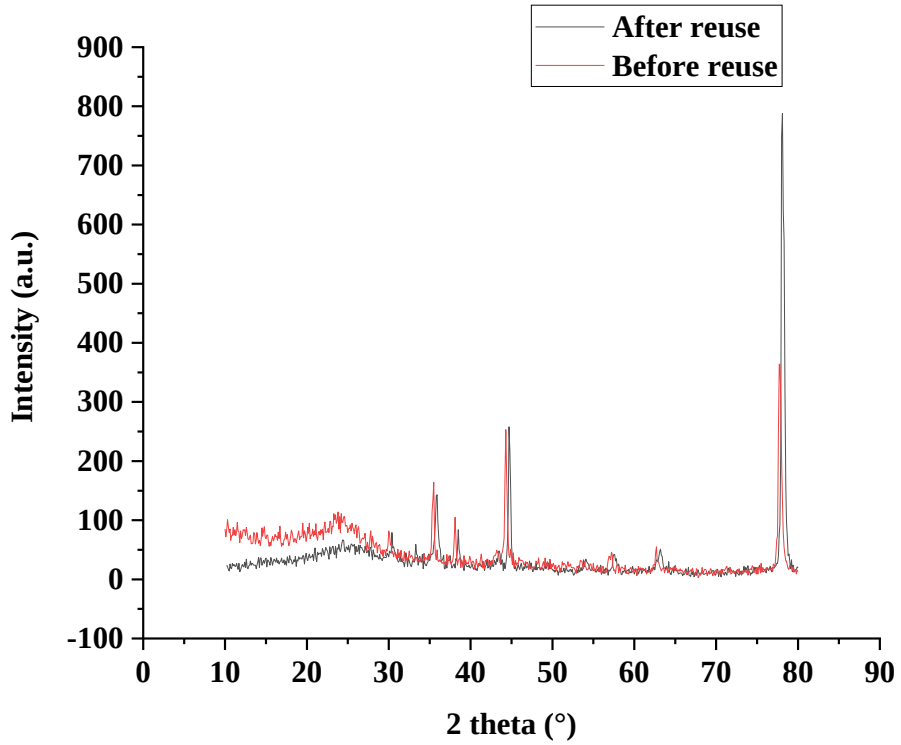


Figure V.27: The provided XRD pattern shows the diffraction data for the magnetic iron nanoparticles (NPs) before and after reuse.

This involves analyzing the NPs that contain methylene blue before reuse and after being regenerated by heating in an oven. Here's a detailed explanation based on the XRD patterns:

1. **Before Reuse (Containing Methylene Blue)**:

- The XRD pattern shows peaks indicating the presence of crystalline phases.
- The peaks are somewhat broad, which could be due to the presence of methylene blue on the surface of the nanoparticles or due to smaller crystallite size.

2. **After Reuse (Post Regeneration)**:

- The XRD pattern after regeneration shows sharper and more defined peaks.
- This indicates that the crystallinity of the nanoparticles is restored or enhanced after the thermal treatment.
- The regeneration process likely removes the adsorbed methylene blue, resulting in clearer peaks associated with the iron oxide phases.

Specific Analysis:

- **Peak Identification**: The primary peaks in both patterns can be matched against standard diffraction patterns of iron oxides to confirm the phases present.

- **Intensity and Peak Shape Changes**: The sharper peaks after reuse indicate improved crystallinity. The broad peaks before reuse suggest the presence of methylene blue, which might obscure some of the diffraction signals.

Detailed Peak Analysis:

- **Before Reuse**: Peaks around 2θ = 30°, 35°, 43°, 57°, and 63° can be associated with the (220), (311), (400), (511), and (440) planes of Fe_3O_4, respectively, though they appear broad due to the adsorbed methylene blue.
- **After Reuse**: The same peaks are present but sharper, indicating the removal of methylene blue and possible improvement in crystallinity due to the thermal treatment at 150°C.

This regeneration process aligns with other studies showing the robustness and reusability of iron oxide nanoparticles in environmental applications. Overall, the synthesized nanoparticles demonstrate great potential as a sustainable solution for water treatment, offering effective contaminant removal with the capability of regeneration and reuse, thereby minimizing environmental impact and operational costs. The consistent 2θ values before and after treatments affirm the structural integrity and stability of the nanoparticles, supporting their repeated use in practical applications **[20]**.

V.6. Test DPPH

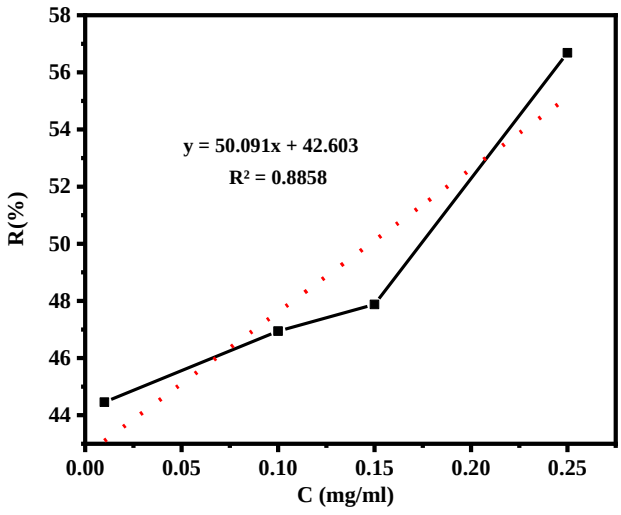


Figure V.28: DPPH free radical inhibition ratio curve R (%) as a function of nanoscale iron oxide concentration (mg/ml).

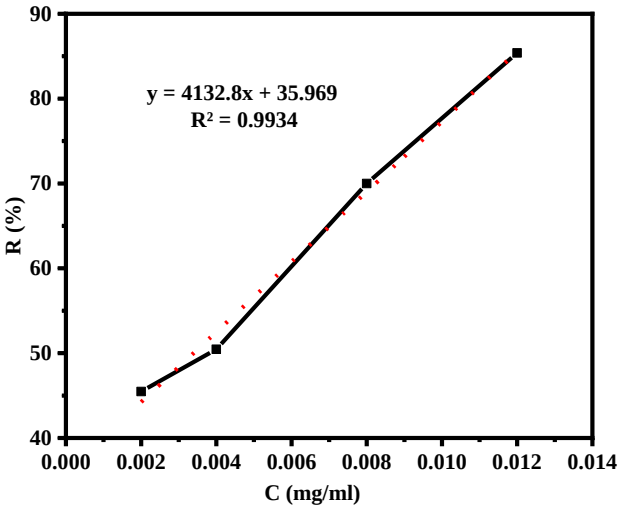


Figure V.29: DPPH free radical inhibition ratio curve R (%) as a function of ascorbic acid concentration (mg/ml).

Using the preceding curves, let compute the RC_{50} values.

	Iron oxide nanoparticles	Ascorbic acid
RC_{50} (mg/ml)	0.174	0.0038

Analysis of findings:

Antioxidants protect cells from reactive oxygen species (ROS), which can cause oxidative damage. Antioxidant activity of iron oxide nanoparticles synthesized from mint leaf extract. It was determined using the DPPH method. The RC_{50} value was used to calculate antioxidant activity. The RC_{50} value shows the concentration of antioxidants required to reduce free radicals by 50%. The lower the RC_{50}, the better the antioxidant scavenging activity of the samples **[21]**.

The results showed the scavenging capacity of the composite iron oxide nanoparticles and standard ascorbic acid for DPPH radical with values of RC_{50} 0.0038 mg/ml and 0.174 mg/ml. Previous studies have proven that iron oxide nanoparticles have excellent antioxidant activities **[22-24]**. Therefore, iron oxide nanoparticles scavenge free radicals by transferring hydrogen atoms or donating electrons to DPPH radicals. As a result, it can stop the oxidation process and prevent oxidative damage to proteins, nucleic acids, carbohydrates and lipids **[25]**. Thus, the potential antioxidant activity of iron oxide nanoparticles could be useful as anti-cancer agents and other harmful diseases in the future **[26]**.

References

1. Markova, I.N., Zahariev, I. Z., Milanova, V. L., Ivanova, D. I., Piskin, M. B., Fachikov, E., and Hristoforou, L. B. (2017). Nanomaterials based on intermetallic (Co-Sn, Ni-Sn, Co-Ni) nanoparticles studied by FTIR spectroscopy. Reviews on Advanced Materials Science, 52(1-2), 70-81.
2. Araújo, C.S.T., Melo, E.I., Alves, V.N., Coelho, N.M.M. (2010). Moringa oleifera Lam. seeds as a natural solid adsorbent for removal of AgI in aqueous solutions, J. Braz. Chem. Soc. 21, 1727–1732.
3. Sakura, G.B., Leung, A.Y.T. (2015). Experimental Study of Particle Collection Efficiency of Cylindrical Inlet Type Cyclone Separator, Int. J. Environ. Sci. Dev.6, 160- 164
4. Khalil, Ali Talha, et al. "Biosynthesis of iron oxide (Fe2O3) nanoparticles via aqueous extracts of Sageretia thea (Osbeck.) and their pharmacognostic properties". Green Chemistry Letters and Reviews 10.4 (2017): 186-201.
5. Karaoğlu, E., Baykal, A., Erdemi, H., Alpsoy, L., Sozeri, H. (2011). Synthesis and characterization of dl-thioctic acid (DLTA)-$Fe3\ O4$ nanocomposite. J. Alloy Compd. 509, 9218-9225.
6. Zhang, Y., Sun, C., Yang, Y., Wang, J., Liu, J., Shi, Q., ... & Xu, Y. (2010). "Crystal Structure and Magnetic Properties of Iron Nanoparticles Synthesized by Chemical Vapor Condensation." Journal of Physical Chemistry C, 114(36), 15446-15452. DOI: 10.1021/jp103479r
7. Rao, C. N., Müller, A., & Cheetham, A. K. (Eds.). (2004). The chemistry of nanomaterials: synthesis, properties and applications (Vol. 1). John Wiley & Sons.
8. Leela, A., & Vivekanandan, M. (2008). Tapping the unexploited plant resources for the synthesis of iron oxide nanoparticles. African Journal of Biotechnology, 7(25).
9. Salim, S., and Timmimi. A. (2017) Characterization of iron nanoparticles preparation frompunicagranatum peel. International Journal of Science and Technology, 8(2), 213-216.
10. Singh, Ashok K. Engineered nanoparticles: structure, properties and mechanisms of toxicity. Academic Press, 2015:538
11. Mallick, P., and B. N. Dash. "X-ray diffraction and UV-visible characterizations of α-Fe2O3 nanoparticles annealed at different temperature." Nanosci. Nanotechnol 3.5 (2013): 130-134.
12. Goyal, Rajendra N., Davinder Kaur, and Ashish K. Pandey. "Growth and characterization of iron oxide nanocrystalline thin films via low-cost ultrasonic spray pyrolysis." Materials Chemistry and Physics 116.2-3 (2009): 638-644.
13. Jawad, A. H., Waheeb, A. S., Rashid, R. A., Nawawi, W. I., & -6Yousif, E. (2018). Equilibrium isotherms, kinetics, and thermodynamics studies of methylene blue adsorption on pomegranate.
14. Omer, O.S., et al., Adsorption thermodynamics of cationic dyes (methylene blue and crystal violet) to a natural clay mineral from aqueous solution between 293.15 and 323.15 K. Arabian Journal of Chemistry, 2018. 11(5): p. 615-623.
15. Jun, Y., Seo, J., Cheon, J., & Lee, J. (2011). "Tuning the Optical and Magnetic Properties of Nanoparticles by Surface Modification." *ACS Nano*, 5(12), 9769-9776. DOI: 10.1021/nn202678d
16. Chen, J., Zhou, S., Huo, D., Xie, S., & Li, W. (2019). "Structure and Magnetic Properties of Iron Nanoparticles Prepared by Hydrogen Reduction." *Journal of Magnetism and Magnetic Materials*, 469, 166022.DOI: 10.1016/j.jmmm.2019.166022

17. Jawad, A. H., Abdulhameed, A. S., Hanafiah, M. M., ALOthman, Z. -9A., Khan, M. R., & Surip, S. N. (2021). Numerical desirability function adsorption of methylene blue dye by sulfonated pomegranate peel for biochar: Modeling, kinetic, isotherm, thermodynamic, and mechanism .1509-38(7), 149938, Korean Journal of Chemical Engineering study.
18. Paramesh, C. C., Halligudra, G., Gangaraju, V., Sriramoju, J. B., Shastri, M., Rangappa, D., ... & Shivaramu, P. D. (2021). Silver nanoparticles synthesized using saponin extract of Simarouba glauca oil seed meal as effective, recoverable and reusable catalyst for reduction of organic dyes. Results in Surfaces and Interfaces, 3, 100005.

19. He, Y., Ma, C., Tang, H., & Yang, Z. (2019). "A Facile Method for Synthesis of Iron Oxide Nanoparticles: FTIR and XPS Characterization." Journal of Colloid and Interface Science, 544, 156-162. DOI: 10.1016/j.jcis.2019.03.012

20. Zhao, X., & Yan, H. (2018). "Effect of Annealing Temperature on the Structural and Magnetic Properties of Iron Nanoparticles Prepared by Sol–Gel Method." Applied Surface Science, 456, 112-117. DOI: 10.1016/j.apsusc.2018.08.245
21. Hazra, B., S. Biswas, and N. Mandal, Antioxidant and free radical scavenging activity of Spondias pinnata. BMC complementary and Alternative Medicine, 2008. 8: p. 1-10.
22. Shah, S.T., et al., Surface functionalization of iron oxide nanoparticles with gallic acid as potential antioxidant and antimicrobial agents. Nanomaterials, 2017. 7(10): p. 306.
23. Tuzun, B.S., et al., Structural characterization, antioxidant and cytotoxic effects of iron nanoparticles synthesized using Asphodelus aestivus Brot. aqueous extract. Green Processing and Synthesis, 2020. 9(1): p. 153-163.
24. Ullah, M., D.-S. Kim, and K.H. Park, Evaluating antioxidant activity of phenolic mediated Fe3O4 nanoparticles using Usnea Longissimma methanol extract. Results in Chemistry, 2022. 4: p. 100661.
25. Iannone, M.F., et al., Impact of magnetite iron oxide nanoparticles on wheat (Triticum aestivum L.) development: evaluation of oxidative damage. Environmental and Experimental Botany, 2016. 131: p. 77-88.
26. Saravanan, M., et al., Emerging plant-based anti-cancer green nanomaterials in present scenario. Comprehensive analytical chemistry, 2019. 87: p. 291-318.

Conclusion

Conclusion

In conclusion, the green synthesis of nanoparticles and their application in water treatment through the phenomenon of adsorption represent a promising and significant field in environmental engineering and sciences. Recent research indicates that this technology is effective in removing a variety of organic and inorganic pollutants from different water sources.

The physicochemical and mineralogical characterization of the synthesized material, magnetic iron NPs showed that all the presence of all the necessary characteristics, and so, it can be concluded that the NPs are well synthezised.

The preliminary study for four distinct dyes was carried out and methylene blue had the highest yield, at 35.7%. Thus, MB was chosen as the pollutant for the rest of the experiences. The photo degradation of MB using magnetic iron NPs has been studied in different conditions: in darkness, under sunlight, and in UV lights. Yields of 79%, 98%, and 99% were achieved in the three previous conditions successively.

The investigation of the kinetic study showed good fit of the experimental results with both pseudo-first and pseudo-second orders, except for the pseudo-first order of the experience in darknes.

The regeneration of the used NPS under severe conditions showed a good reuse after four cycles. This result can be studied with more details.

All the statistical study of the adsorption showed good ANOVA of the three studied responses which are A, R, and q. The three models can be used for further studies.

A good prediction of the three models can be noticed in terms of regression coefficients (R^2, R^2 adjusted, and R^2 predicted).

In conclusion, the findings of this work research demonstrate the viability of green synthesis using Mentha *spicata* extract for the synthesis of magnetic iron Nnanoparticles, offering promising prospects for their application in diverse fields.

Future perspectives

- Study the optimization of the green synthesis of the nanoparticles.
- Explore other types of plants.
- Elaboration of novel composites.
- Expand the study for another types of pollutants.

Appendices

Mint leaves before washing

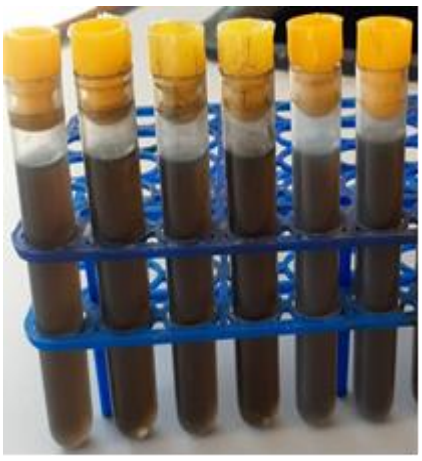
Mint leaves after washing and drying

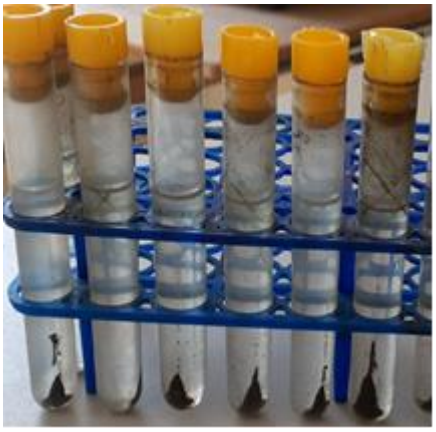
Crushed mint leaves

Abstract

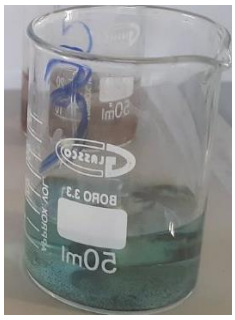
Filtration process

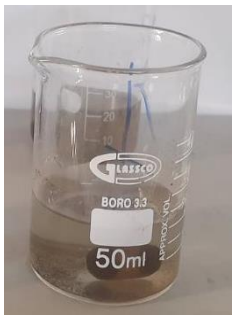
FeCl3 solution

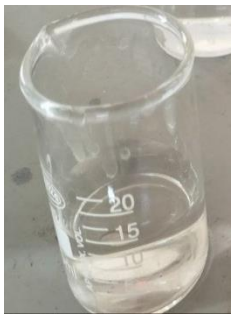




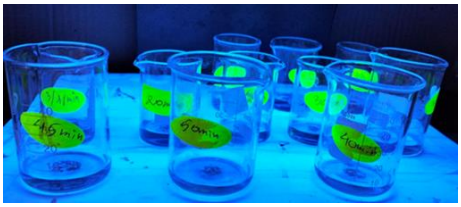
Nano fabrication process





Stages of treating polluted water



Water treatment under UV light

Water treatment under sunlight

Sensitive electronic scale

Oven (thermal incubator)

X-ray diffraction machine

UV spectrophotometer

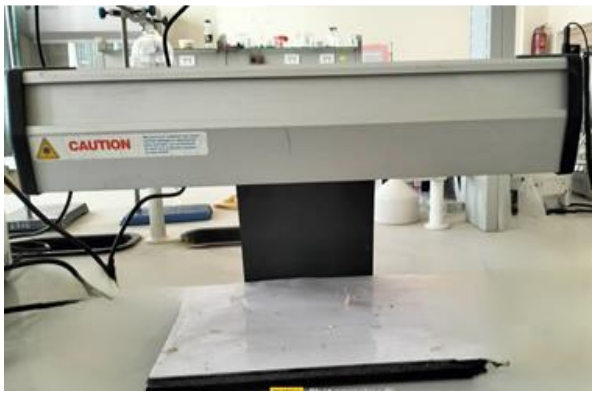
Ultrasound device

Scanning electron microscop) SEM-EDX (

Centrifuge

pH meter device

FTIR infrared spectrometer



Scanning electron microscope (SEM-EDX) **UV light device**

الجمهورية الجزائرية الديمقراطية الشعبية

وزارة التعليم العالي و البحث العلمي

جامعة: الشهيد حمه لخضر – الوادي-

Using Medicinal Plant Extract for the Green Synthesis of Magentic Nanoparticles Intended for Polluted Water Remediation :Optimization and Insight

مشروع لنيل شهادة مؤسسة ناشئة في اطار القرار الوزاري 1275

PUREWAVE

PUREWAVE
Water Treatment

بطاقة م ومات:

حول فر الاشراف وفريق العمل

1- يق الاشراف:

فريق الاشراف	
المشرف الرئيسي: **العربي حداد**	**التخصص:** **كيمياء المواد**

2- يق العمل:

فريق المشروع	التخصص	الكلية
الطالبة: بروبه كوثر	كيمياء عضوية	العلوم الدقيقة
الطالبة: هميسي صفاء	كيمياء عضوية	العلوم الدقيقة
الطالبة: حمصي منار	كيمياء عضوية	العلوم الدقيقة
الطالبة: دقله ذكرى منال	كيمياء عضوية	العلوم الدقيقة

فهرس المحتويات

المحور الأول: تقديم المشروع:

Using Medicinal Plant Extract for the Green Synthesis of Magentic Nanoparticles Intended for Polluted Water Remediation :Optimization and Insight.

1. فكرة المشروع (الحل المقترح)

يقدم PureWave حّلا جديدا لمعالجة المياه الملوثة باستخدام مستخلص نبات طبي والحد الأدنى من المواد الكيميائية غير المؤذية و ذات الإستهلاك البشري ، فإنه ينقي المياه بشكل فعال للاستهلاك والاستخدام ، مما يجعله حلاً مستدامًا وصديقًا للبيئة. جعلنا الحل في صيغته النهائية على شكل أكياس صغيرة محمولة وسهلة الاستخدام ، فهي ملائمة للتطبيق الفوري و مثالية لحالات الطوارئ.

2. القيم المقترحة

أكياس معالجة المياه الملوثة:

- من مصدر طبيعي وآمن
- صديقة للبيئة
- سهلة الحمل
- سهلة الاستعمال
- فعالة ومستدامة

3. فريق العمل

الطالبة: بروبه كوثر

الطالبة: حمصي منار

الطالبة: هميسي صفاء

الطالبة: دقلة ذكرى منال

4. أهداف المشروع :

- ✓ الحصول على مياه نقية
- ✓ تلبية احتياجات المجتمع في مجال معالجة المياه
- ✓ الحد من تأثيرات التلوث و حماية البيئة
- ✓ تحقيق التنمية المستدامة و الاستدامة الاجتماعية والبيئية في المنطقة

5. جدول زمني لتحقيق المشروع :

		شهر							
الترتيب الزمني	**المهمة**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	**الدراسة الأولية للمشروع: إختيار مقر الوحدة ، تحضير الوثائق الإدارية.**	×							
2	**طلب مختلف التجهيزات**	×	×	×	×				
3	**بناء مقر الوحدة**		×	×	×	×			
4	**تركيب المعدات المطلوبة**						×	×	
5	**اقتناء المواد الأولية**		×	×	×				
6	**بداية إنتاج أول حصة**								×

المحور الثاني: الجوانب الابتكارية

تتمثل الجوانب الابتكارية في مشروعنا في كونه :

- ✓ اول مشروع في الجزائر يعتمد على استخدام أكسيد الحديد النانوي في تنقية المياه الملوثة
- ✓ تثمين نبات الطبي (النعناع) (المادة الأولية لتخليق أكسيد الحديد النانوي) في معالجة المياه
- ✓ استهداف فئة جديدة من المستهلكين (قطاع الزراعي ،الصناعات ،القطاع المنزلي و القطاع البيئي).

المحور الثالث: التحليل الاستراتيجي للسوق

1- عرض القطاع السوقي:

الشرائح المستهدفة:

"نحدد الشرائح المستهدفة بعناية لمؤسستنا التي تعنى بمعالجة المياه باستخدام مادة نانوية . إليك وصفًا للشرائح المستهدفة:

المؤسسات الحكومية: نستهدف الجهات الحكومية المسؤولة عن معالجة المياه والصرف الصحي في المناطق الصحراوية. نقدم لهم حلولًا مستدامة وفعالة لتحسين جودة المياه وتوفير مصادر محلية للمواد الماصة المستخدمة في المعالجة.

الشركات والمؤسسات الصناعية: نستهدف الصناعات المختلفة التي تولد مياه ملوثة وتحتاج إلى تصفيتها وتنقيتها. نقدم لهم تقنية الامتزاز باستخدام أكسيد الحديد النانوي كحلاً فعالًا ومستدامًا لمعالجة مياههم.

البلديات والهيئات المحلية: نستهدف البلديات والهيئات المحلية في المناطق الصحراوية، حيث يكون لديهم تحديات في توفير المياه النقية والنظيفة للمجتمعات. نقدم لهم حلولًا معالجة مياه مستدامة وفعالة لتلبية احتياجات سكان المنطقة.

الشركات الزراعية ومزارع النباتات : نستهدف الشركات الزراعية ومزارع النباتات الطبية التي تولد نبتة النعناع والتي تمثل المادة الاولية لتحضير جسيمات أكسيد الحديد النانوي. نقدم لهم دافعا لزيادة إنتاج وزرع هذا النوع من النبات والإستفادة منها في عملية معالجة المياه.

الجهات البحثية والأكاديمية: نستهدف الجهات البحثية والأكاديمية المهتمة بمجال معالجة المياه والاستدامة. نتعاون معهم في إجراء البحوث وتطوير التقنيات وتبادل المعرفة. يمكننا أن نقدم لهم المواد الخام والمعلومات الفنية لدعم أبحاثهم وتحقيق التقدم في هذا المجال.

من خلال استهداف هذه الشرائح المستهدفة المختلفة، نهدف إلى تلبية احتياجاتها المحددة وتقديم حلول مبتكرة وفعالة لمشاكل معالجة المياه. سنعمل على توسيع شبكة عملائنا وبناء علاقات طويلة الأمد معهم لتحقيق نمو مستدام ونجاح لمؤسستنا.

2- قياس شدة المنافسة:

أ- المنافسون المباشرون:

شركات معالجة المياه الأخرى في نفس المنطقة أو المجال.

ب- أعداد المنافسين المباشرين:

يتنوع عدد المنافسين حسب المنطقة والسوق المستهدفة. يجب إجراء دراسة السوق المستهدفة لتحديد الأعداد الدقيقة للمنافسين.

الجهات الحكومية أو المؤسسات ذات الصلة التي تعمل في مجال معالجة المياه وحماية البيئة

ت- نقاط ضعف المنافسين المباشرين:

- قد يفتقر بعض المنافسين إلى التقنيات الحديثة والابتكارات الجديدة في معالجة المياه.
- قد يواجه بعضهم صعوبة في توفير حلول مستدامة واقتصادية.
- قد يكون لديهم قيود مالية أو تقنية تؤثر على القدرة على تنفيذ مشاريع كبيرة

ث- نقاط قوة المنافسين المباشرين:

خبرة عملية في مجال معالجة المياه وتقنياتها.

3- الاستراتجيات التسويقة:

- تحديد السوق المستهدف :

قم بتحليل وتحديد القطاعات والصناعات التي تحتاج بشكل خاص إلى خدمات معالجة المياه والتركيز على هذه السوق المحددة.

- تسويق المزايا التنافسية:

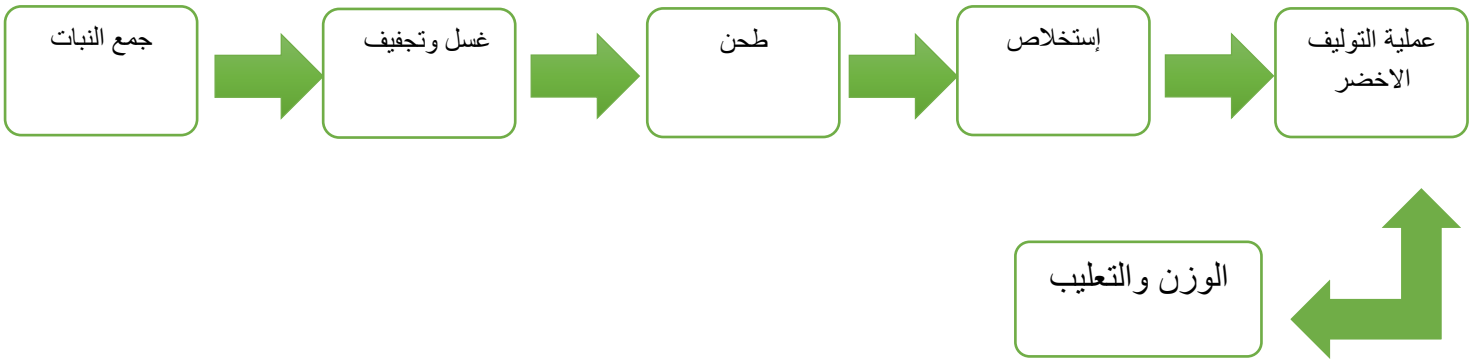
قم بتسليط الضوء على المزايا التنافسية الفريدة لمشروعك، مثل استخدام النبات الطبية كمصدر متجدد لمعالجة المياه الملوثة. أبرز الفوائد البيئية والاقتصادية لاستخدام تقنية مبتكرة ومستدامة.

- الشراكات والتعاون :

بناء علاقات قوية مع الشركات والمؤسسات ذات الصلة والجهات الحكومية لتعزيز التعاون في مجال معالجة المياه. قم بتطوير شراكات استراتيجية مع موردي المواد الخام والشركات المهنية المتخصصة في مجال المياه.

المحور الرابع:خطة الإنتاج والتنظيم

1. عملية الإنتاج:



2. التموين:

التموين هو عملية تأمين المواد والموارد اللازمة لسير العمليات اليومية للمشروع. وفيما يلي بعض النقاط التي يمكن الكتابة عنها بخصوص التموين والعناصر المذكورة:

- تحديد سياسة الشراء:

تحديد سياسة الشراء هو عملية تحديد الإجراءات والمعايير التي يتم اتباعها لاختيار وشراء المواد والموارد المطلوبة. يمكن الكتابة عن معايير اختيار الموردين، وعملية المناقصة إذا كانت مطبقة، وضوابط الجودة والمواصفات المطلوبة للمواد المشتراة.

- تحديد أهم الموردين:

تحديد أهم الموردين يتطلب تقييم مجموعة من العوامل مثل الجودة، والسعر، والتوافر، والتسليم في الوقت المحدد. يمكن الكتابة عن استراتيجيات تطوير العلاقات مع الموردين الرئيسيين وضمان توفر المواد والخدمات المطلوبة بشكل مستمر.

- تحديد سياسة الدفع ووقت الاستلام:

تحديد سياسة الدفع ووقت الاستلام يتعلق بالشروط التجارية بين المشروع والموردين. يمكن الكتابة عن سياسات الدفع المعتمدة، مثل الدفع المسبق أو الدفع بعد التسليم، وكذلك تحديد وقت الاستلام المطلوب والمتوقع لضمان استمرارية العمليات دون تأخير.

يمكنك توسيع النقاط المذكورة وتضمين المزيد من التفاصيل والاستراتيجيات الملائمة لمشروعك والسوق الذي تعمل فيه.

3. اليد العاملة:

- عدد المناصب:

نحن نعمل على تحديد عدد المناصب الوظيفية المناسبة لمشروعنا. سيتم تحديد العدد الدقيق بناءً على احتياجات العمل والقدرات المتاحة. نريد أن نضمن توافر اليد العاملة الكافية لتنفيذ عمليات المعالجة بكفاءة وفقًا لمعايير الجودة المطلوبة.

- طبيعة ونوعية اليد العاملة:

نحرص على اختيار اليد العاملة ذات المهارات والخبرات الملائمة لمشروعنا. نحتاج إلى فريق يتمتع بالمعرفة والخبرة في مجال تلوث المياه ومعالجتها. يجب أن يكون لديهم فهم عميق للتقنيات والعمليات المستخدمة في معالجة المياه الملوثة. نحن نبحث عن فريق ملتزم بالجودة والمسؤولية والتحسين المستمر.

- إمكانية اللجوء إلى المناول :

نحن ندرس إمكانية استخدام المناولة في عملياتنا. يعتبر استخدام المناولة وسيلة فعالة لتحسين كفاءة العمل وتقليل الجهد البشري المباشر. سنقوم بتحليل عملياتنا وتحديد النقاط التي يمكن فيها استخدام المناولة بشكل أكثر فائدة وتحقيق توفير في التكاليف والزمن.

4. الشراكات الرئيسية :

الشراكات الرئيسية تعد جزءًا حاسمًا في نجاح مشروعنا وتمكيننا من تحقيق أهدافنا. وفيما يلي بعض الشراكات الرئيسية المهمة بالنسبة لنا:

- الشراكات مع المزارعين :

نحن نسعى للتعاون مع المزارعين ومنتجي النباتات الطبية للحصول عليها كمصدر رئيسي لعملياتنا. يمكننا توقع الحصول على النبات الطبي(النعناع) المطلوب بكميات كافية وبجودة ملائمة لعملياتنا. يتطلب هذا التعاون إقامة شراكات استراتيجية لضمان التزويد المستدام بالمواد الخام اللازمة.

- الشراكات مع الجهات الحكومية والبيئية:

يجب علينا التعاون مع الجهات الحكومية والبيئية المختصة لضمان الامتثال للوائح والقوانين البيئية المحلية والدولية. يمكننا العمل مع الجهات الحكومية في تبادل المعلومات والاستفادة من الدعم والموارد المتاحة لتعزيز عملياتنا وتحقيق التوازن بين الجوانب البيئية والاقتصادية.

- الشراكات مع الشركات الموردة للتجهيزات والمعدات:

قد نحتاج إلى الاعتماد على شركات توريد التجهيزات والمعدات اللازمة لعمليات المعالجة. يجب أن تكون هناك شراكات موثوقة مع الشركات الموردة ذات الخبرة والسمعة الجيدة في توفير المعدات عالية الجودة والتكنولوجيا المتقدمة لمشروعنا.

- الشراكات مع العملاء والمستفيدين:

نحن نسعى لتطوير علاقات قوية مع العملاء والمستفيدين لمشروعنا. يجب علينا تحديد احتياجاتهم وتقديم الحلول المناسبة لتلبية متطلباتهم في مجال معالجة المياه الملوثة. يمكننا أن نعمل مع العملاء على تحقيق الاستدامة والتوعية بأهمية المحافظة على البيئة وتحسين جودة المياه.

- الشراكات الأكاديمية والبحثية:

نحن نتطلع إلى التعاون مع المؤسسات الأكاديمية والبحثية للاستفادة من الخبرة والخبرات في مجال معالجة المياه وتحقيق التقدم التكنولوجي. يمكن أن تشمل هذه الشراكات تبادل المعرفة والبحث المشترك وتطوير التقنيات الجديدة التي يمكن تطبيقها في مشروعنا.

المحور الخامس: الخطة المالية PLAN FINANCIER

1. التكاليف والأعباء:

- تحديد التكاليف بدقة:

نحن نعمل على تحديد التكاليف بدقة وشمولية. يجب أن نضع في اعتبارنا جميع العناصر التكاليفية المرتبطة بالمشروع، بما في ذلك تكاليف المواد الخام، وتكاليف التجهيزات والمعدات، وتكاليف العمالة، والتكاليف الإدارية، والتكاليف التشغيلية، وتكاليف التسويق والترويج. يجب أن نكون دقيقين في تقدير هذه التكاليف لضمان استدامة المشروع وتحقيق العائد المرجو.

- طرق ومصادر الحصول على التموين:

يتطلب مشروعنا التوفر المستدام على التموين اللازم لعملياتنا. سنعمل على تحديد أفضل طرق ومصادر الحصول على التموين بأسعار تنافسية وجودة مطابقة للمعايير. يمكن أن تشمل طرق الحصول على التموين التعاقد مع موردين موثوقين، أو التعاون مع المزارعين والشركات الزراعية المنتجة لنباتات الطبية المطلوبة. سنسعى أيضًا إلى التفاوض على عقود واتفاقيات طويلة الأجل لضمان استدامة التموين.

- جدول العوائد:

سنقوم بإعداد جدول للعوائد المتوقعة من مشروعنا. سيتم تحليل وتقدير العوائد المالية المحتملة على المدى القصير والمتوسط والطويل. يجب أن يشمل جدول العوائد تقديرات دقيقة للإيرادات المتوقعة من عمليات المعالجة ومبيعات المنتجات المتعلقة.

2. رقم الاعمال :

- إجمال المبيعات:

فيما يتعلق برقم الأعمال، يعد إجمالي المبيعات أحد العوامل الرئيسية التي تحدد نجاح المشروع وتحقيق العائد المالي المرجو. يتعين علينا تحديد توقعات وتقديرات دقيقة لإجمالي المبيعات المتوقعة بناءً على دراسة السوق وتحليل الطلب والعرض.

- وجهتا النظر التفاؤلية والتشاؤمية:

~ وجهة النظر التفاؤلية:

ترى أن هناك فرصًا كبيرة لنمو الطلب على خدماتنا ومنتجاتنا في سوق معالجة المياه الملوثة. يمكن أن يؤدي التوجه العالمي نحو الاستدامة وحماية البيئة إلى زيادة الاهتمام بحلول مبتكرة وصديقة للبيئة لمعالجة التلوث المائي. تعتقد أن مشروعنا سيكون ناجحًا ويحقق أرباحًا مجزية في المستقبل.

~ وجهة النظر التشاؤمية:

تعتبر أن السوق قد يكون تنافسيًا بشكل كبير وأن هناك صعوبات في الوصول إلى العملاء والتنافس مع الشركات الموجودة في السوق. ترى أن التحديات التقنية والبيئية والاقتصادية يمكن أن تؤثر سلبًا على عملياتنا وتقلل من إمكانية تحقيق العائد المالي المتوقع.

3. جدول حسابات الناتج المتوقع :

- جدول مالي يلخص اجمالي المبيعات والأعباء:

يجب أن يتم إعداد جدول مالي يلخص إجمالي المبيعات والأعباء لمشروعنا. هذا الجدول سيشمل التفاصيل المالية الرئيسية مثل إجمالي المبيعات المتوقعة في فترات زمنية معينة والتكاليف العامة والمتغيرة المرتبطة بالمشروع. يمكن استخدام هذا الجدول لتحديد الإيرادات والتكاليف المتوقعة وحساب الربحية المحتملة وتقدير الأرباح والخسائر.

- حساب احتياجات رأس المال العام:(BFR)

يجب أن نقوم بحساب احتياجات رأس المال العام (BFR) لمشروعنا. يشير BFR إلى الاحتياجات المالية لتمويل دورة التشغيل للمشروع، بما في ذلك شراء المواد الخام والمخزون، وتسديد المستحقات المالية للموردين، وتغطية تكاليف العمالة والتشغيل اليومي. يتطلب حساب BFR تحليل دقيق للتدفقات المالية والأنشطة التشغيلية لتحديد الاحتياجات المالية الفعلية وتوقع التغيرات في رأس المال العام لدينا.
هذه الحسابات والجداول المالية الدقيقة تساعدنا في فهم وتقييم الأوضاع المالية لمشروعنا وتحديد الاحتياجات المالية وتخطيط الاستثمارات بشكل فعال لضمان استدامة المشروع وتحقيق العائد المرجو.

4. خطة الخزينة:

- تقديرات التدفقات النقدية:

يتعين علينا تحديد التدفقات النقدية المتوقعة للمشروع على مدى فترة زمنية محددة. يجب أن نأخذ في الاعتبار الإيرادات المتوقعة من المبيعات، وتكاليف الإنتاج والتشغيل، والتكاليف الإدارية والتسويقية، والتدفقات النقدية الأخرى المرتبطة بالمشروع.

- تحديد الاحتياجات النقدية:

يجب أن نحدد الاحتياجات النقدية الفعلية للمشروع. هذا يشمل تحديد التكاليف المستدامة والمتغيرة وأوقات الدفع المستحقة للموردين والمصروفات الشهرية العامة وأية التزامات أخرى تتطلب سيولة نقدية.

- إدارة التدفقات النقدية:

يجب علينا وضع استراتيجية لإدارة التدفقات النقدية بشكل فعال. يمكن أن تشمل هذه الاستراتيجية تحسين عملية التحصيل وتقديم خدمات العملاء، وإدارة الدفعات للموردين، وتوفير حلول لتمويل الاحتياجات النقدية القصيرة الأجل.

- رصد الأداء المالي:

يتعين علينا مراقبة ورصد الأداء المالي للمشروع وتقييمه بانتظام. يتضمن ذلك مقارنة التدفقات النقدية الفعلية مع التوقعات، وتحليل الانحرافات واتخاذ التدابير اللازمة إذا لزم الأمر.

توفير خطة الخزينة الصحيحة يمكن أن يساعدنا على تجنب نقص السيولة المالية والتأكد من توافر التمويل اللازم لتشغيل المشروع بسلاسة. يجب تحديث ومراجعة خطة الخزينة بانتظام لضمان أنها تعكس التغيرات في الظروف المالية وتتوافق مع استراتيجيات المشروع.

المحور السادس : النموذج الاولي التجريبي

➢ الجداول والأشكال

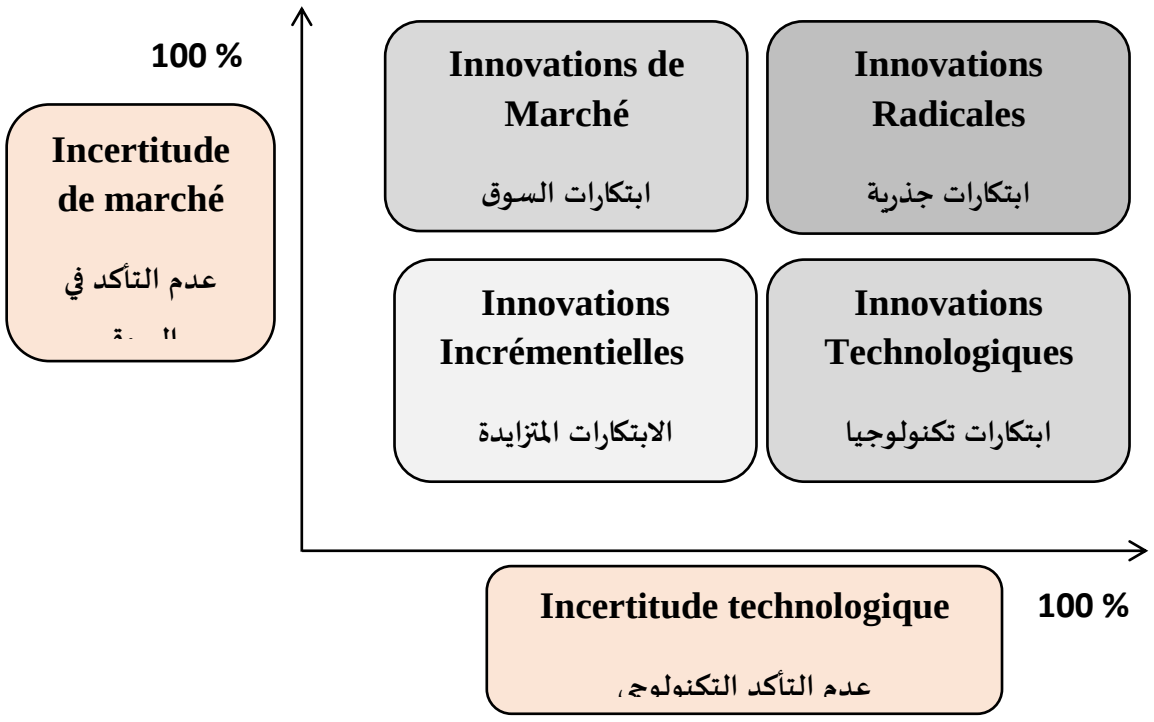
الجدو ل(01): .....

STARTUP : .....

	REALISATION			PREVISION				
Produit A destiné Client	**N -2**	**N -1**	**N**	**N+1**	**N+2**	**N+3**	**N+4**	**N+5**
Quantité produit A	**3000**	**3300**	**3630**	**3993**	**4392**	**4831**	**5314**	**5845**

Prix HT produit A	6	6	6	6	6	6	6	6
Ventes produit A	-	-	-	-	-	-	-	-
CHIFFRE D'AFFAIRES GLOBAL	18 000	1 9800	21780	23958	**26354**	**28989**	**31888**	**35076**

الشكل(01): .....



قائمة الملاحق :

الملحق رقم 01: ميزانية المؤسسة الناشئة

BILANS DE STARTUP : .....

ACTIF								
	REALISATION			PREVISION				
En milliers DZD	N -2	N -1	N	N+1	N+2	N+3	N+4	N+5
Immobilistation Incorporelles	-	-	-	-	-	-	-	-
Immobilisation Corporelles	-	-	-	-	-	-	-	-
Terrain								
Bâtiment	5000	5000	5000	5000	5000	5000	5000	5000
Autres Immobilisations Corporelles	10000	10000	10000	10000	10000	10000	10000	10000
Immobilisations en concession								
Immobilisation en cours	-	-	-	-	-	-	-	-
Immobilisations Financières	-	-	-	-	-	-	-	-
Titres mis en équivalence								
Autres participations et créances rattachées								

Autres Titres immobilisés								
Prets et autres titres financiers non courants								
Impôts différés actif								
ACTIF NON COURANT	**15000**	**15000**	**15000**	**15000**	**15000**	**15000**	**15000**	**15000**
Stocks et encours	-	-	-	-	-	-	-	-
Créances et emplois assimilés	-	-	-	-	-	-	-	-
Clients								
Autres débiteurs								
Impôts et assimilés								
Autres créances et emplois assimilés								
Disponibilités et assimilés	-	-	-	-	-	-	-	-
Placements et autres actifs financiers courants								
Trésorerie	5000	**8125**	**11750**	**15925**	**20705**	**26151**	**32312**	**39297**
ACTIF COURANT	5000	**8125**	**11750**	**15925**	**20705**	**26151**	**32312**	**39297**
TOTAL ACTIF	**20000**	**23125**	**26750**	**30925**	**35705**	**41151**	**47312**	**54297**

PASSIF								
	REALISATION			PREVISION				
En milliers DZD	N -2	N -1	N	N+1	N+2	N+3	N+4	N+5
CAPITAUX PROPRES								
Capital émis	0.00							
Capital non appelé								
Ecart de réevaluation								
Primes et réserves- Réserves Consolidées								
Résultat net- RN part du groupe	-	3 125	3625	4175	4780	5446	6161	6985
Autres capitaux propores- report à nouveau								
Part de la société consolidante (1)								
CAPITAUX PROPRES		-	-	-	-	-	-	-
PASSIFS NON-COURANTS								
Emprunts et dettes financières	20000							
impôt différé passif								

Autres dettes non courantes								
Provisions et produits constatés d'avance								
PASSIFS NON-COURANTS	**20000**	**-**	**-**	**-**	**-**	**-**	**-**	**-**
PASSIFS COURNATS								
Fournisseurs et comptes rattachés								
Impôts								
Autres dettes								
Trésorerie passif	**20000**	**23125**	**26750**	**30925**	**35705**	**41151**	**47312**	**54297**
PASSIFS COURANTS	**20000**	**-**	**-**	**-**	**-**	**-**	**-**	**-**
TOTAL PASSIF	**20000**	**23125**	**26750**	**30925**	**35705**	**41151**	**47312**	**54297**
Verification de l'équilibre Actif/Passif	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**

الملحق رقم 02: جدول حسابات النتائج المتوقعة

COMPTE DE RUSULTAT PREVISIONNELDE STARTUP : .....

	REALISATION			PREVISION				
En Milliers DZD	N -2	N -1	N	N+1	**N+2**	**N+3**	**N+4**	**N+5**

Vente et produits annexes	18 000	1 9800	21780	23958	**26354**	**28989**	**31888**	**35777**
Variation des stocks produits finis et en cours								
Production immobilisée								
Subvention d'exploitation								
Production de l'exercice	18 000	1 9800	21780	23958	**26354**	**28989**	**31888**	**35777**
Achats consommés	6000	6600	7260	7986	**8785**	**9663**	**10629**	**11692**
Services Extèrieurs et autres consommations	600	660	726	798	**878**	**966**	**1063**	**1169**
Consommation de l'exercice	6 600	7260	7986-	8785	**9663**	**10629**	**11629**	**12861**
Valeur ajoutée d'exploitation	11400	12540	13794	15173	**16691**	**18360**	**20196**	**22916**
Charges de personnel	6000	6600	7260	7986	**8785**	**9663**	**10629**	**11692**
Impôts et taxes et versement assimilés								
Excédent Brut d'Exploitation	5 400	5940	6534	7187	**7906**	**8697**	**9567**	**11224**
Autres produits opérationnels	400	440	484	532	**585**	**643**	**707**	**778**

Autres charges opérationnelles								
Dotations aux amortissements, Provisions	1 875	1 875	1 875	1 875	1 875	1 875	1 875	1 875
Reprise sur pertes de valeurs et provisions								
Résultat opérationnel	**3 125**	**3625**	**4175**	**4780**	**5446**	**6161**	**6985**	**8571**
Produits Financiers								
Charges financières								
Résultat financier	-	-	-	-	-	-	-	-
Résultat Ordinaire avant impôt	**3 125**	**3625**	**4175**	**4780**	**5446**	**6161**	**6985**	**8571**
Impôt exigible sur résultat ordinaire								
Impôt différé (variation) sur résultat ordinaire								
TOTAL DES PRODUITS DES ACTIVITES ORDINAIRES	18 000	1 9800	21780	23958	**26354**	**28989**	**31888**	**35777**
TOTAL DES CHARGES DES ACTIVITES ORDINAIRES	***14 875***	***16175***	***17605***	***19178***	***20908***	***22828***	***24903***	***27206***

RESULTA NET DES ACTIVITES ORDINAIRES	3 125	3625	4175	4780	5446	6161	6985	8571
Eléments extraordinaire (produits)								
Eléments extraordinaire (charges)								
Résultat extraordinaire	-	-	-	-	-	-	-	-
RESULTAT NET DE L'EXERCICE	3 125	3625	4175	4780	5446	6161	6985	8571

الملحق رقم 03: حسابات الخزينة

TABLEAUX DE FLUX DE TRESORERIE

STARTUP : .....

نقاط القوة :

1-النهج المبتكر: يعد إستخدام Mentha spicata للتخليق الأخضر لجزئيات الحديد النانوية المغناطيسية طريقة للإستفادة من المستخلصات النباتية الطبيعية بما يتماشى مع مبادئ الكيمياء الخضراء .

2-الإستدامة البيئية :تقلل هذه الطريقة من إستخدام المواد الكيميائية الخطرة والعمليات كثيفة الإستهلاك للطاقة ،مما يقلل من المخاطر البيئية والصحية المرتبطة بتخليق الجسيمات النانوية التقليدية .

3-الوظيفة المزدوجة لنبات Mentha spicata : تعمل مركبات النعناع النشطة بيولوجيا كعوامل إختزال وتثبيت ،مما قد يؤدي إلى تحسين جودة وإستقرار الجسيمات النانوية .

4-الخواص المغناطيسية : إن سهولة فصل جزئيات الحديد النانوية المغناطيسية باستخدام مجال مغناطيسي خارجي يزيد من التطبيق العملي وكفاءة عملية المعالجة .

5-التوصيف الشامل: تستخدم الدراسة تقنيات تحليلية متقدمة (FTIR, SEM,XRD,UV-VIS) لتوصيف الجسيمات النانونوية المركبة بدقة مما يوفر فهما تفيليا لخصائصها .

6-التحديات العالمية :إن معالجة المياه قضية عالمية مهمة تؤكد على أهمية هذا البحث وتأثيره المحتمل .

نقاط الضعف:

1-المرحلة الناشئة من البحث: لايزال تطبيق جسيمات الحديد النانوية المغناطيسية الخضراء المركبة في معالجة المياه في مراحله المبكرة ،مع محدودية الأبحاث الحالية التي يمكن البناء عليها .

2-تحديات التوسع: قد يمثل التحول من التخليق على نطاق المختبر إلى الإنتاج الصناعي تحديات بما بما في ذلك الحفاظ على الإتساق والكفاءة .

3-نطاق محدود : تركز الدراسة على مستخلص نباتي محدد ونوع جسيمات متناهية الصغر مما قد يحد من إمكانية تعميم النتائج على نباتات أو جسيمات نانوية أخرى .

الفرص:

1-التنمية المستدامة: يساهم البحث في تطوير تقنيات معالجة المياه الصديقة للبيئة ،وهو مجال إهتمام متزايد في العلوم البيئية والصناعة .

2-التوسع في طرق التخليق الأخضر: النجاح في إستخدام Mentha spicata يمكن أن يشجع على إستكشاف مستخلصات نباتية أخرى مما يوسع نطاق طرق التخليق الأخضر.

3-التعاون والتمويل : إمكانية التعاون البيئة مع و قد ركزت الوكالات والمنظمات الغير حكومية والصناعات على التكنولوجيات المستدامة مما قد يؤدي إى مويل ودعم إضافيين .

4-التقدم التكنولوجي: يمكن للتقدم في التكنولوجيا النانو والتقنيات التحليلية أن يزيد من تعزيز عملية تصنييع وتوصيف الجسيمات النانوية .

5-التأثير على السياسيات والتنظيم : يمكن أن تؤثر النتائج على السياسات واللوائح البيئية مما يعزز إعتماد تكنولوجيا النانو الخضراء في التطبيقات الصناعية .

التهديدات

1-المنافسة: قد تشكل طرق معالجة المياه التقليدية والجسميات النانوية المتوفرة تجاريا منافسة مما قد يؤثر على إعتماد البدائل الخضراء المركبة .

2-العقبات التنظيمية : قد يواجه إدخال المواد النانوية الجديدة تدقيقا تنظيما صارما مما قد يؤدي إلى إبطاء العملية

3-الجدوى الإقتصادية: يجب إثبات فعالية التوليف الأخضر مقارنة بالطرق التقليدية لضمان تكلفة الجدوى الإقتصادية

5-قبول السوق: قد يكون الحصول على قبول السوق للتكنولوجيا الحديثة أمرا صعبا لاسيما في القطاعات ذات الممارسات والتقنيات التقليدية الراسخة .

الملحق رقم 04: نموذج العمل التجاري

الشركاء الأساسيون

- مزارعي نبتة النعناع
- مؤسسات معالجة المياه
- المستثمرون
- مؤسسات التوصيل
- مؤسسات التجهيزات المخبرية و المواد الكيميائية

المهام الأساسية

- اقتناء نبتة النعناع
- تصميم و بناء الوحدة
- الإنتاج
- التعليب و التغليف
- التسويق

المصادر الأساسية

- أوراق النعناع
- موارد مالية
- موارد بشرية
- تكنولوجيا و معدات

القيمة الأساسية

أكياس المعالجة السريعة للماء الملوث:

- طبيعية
- صديقة للبيئة
- سهلة الحمل
- سهلة الاستعمال
- مستدامة
- الخاصية المغناطيسية

العلاقة مع العملاء

- تحليل احتياجات العملاء
- تقديم حلول مخصصة
- الدعم الفني وخدمة العملاء
- بناء علاقة طويلة الأمد
- التحسين المستمر للمنتوج

القنوات

- الموقع الإلكتروني
- الرقم الأخضر
- وسائل التواصل الاجتماعي
- البريد الإلكتروني
- العروض و المعارض
- الدعاية و الإعلانات
- التواصل المباشر

الشرائح المستهدفة

- الشركات الزراعية
- المزارع و الغيطان
- المؤسسات الحكومية
- الشركات و المؤسسات الصناعية
- الهيئات الدولية و غير الحكومية
- المنتزهات المائية و المسابح

هيكلة التكاليف

- تكاليف الإنتاج و التشغيل
- تكاليف الترويج و التسويق

مصادر الدخل

- التمويل و الدعم الحكومي
- الاستشارات الفنية و اللوجستية

PUREWAVE

Water Treatment