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Contribution to the Study of the Photocatalytic Efficacy of Some Metal Oxides in the Removal of Organic Pollutants

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Dedication

And their last word is that praise is due to Allah, the Lord of the Worlds.

All praise is due to Allah, the Lord of the Worlds, from the beginning to the end. No path is completed, no effort is fulfilled, and no pursuit is accomplished except by His grace. The journey was not short, nor was it meant to be. The dream was not close, and the road was not paved with ease, but I did it and I achieved it.

With all my love, I dedicate my graduation thesis:

To my strong self who endured all the stumbling blocks and continued despite the difficulties.

To those whose prayers were the secret of my success, to the one who was a light to me in my darkness, "my mother" ***Safia lekhoua*** *" I dedicate this achievement to you, which would not have been realized without your sacrifices.*

To those who supported me without limits and gave me without asking for anything in return, "my father" ***Abdel-Ali Bahi*** *", this is the least I can give you in return for your generosity.*

*To those in whom it is said: We will strengthen your arm with your brother, to my brothers, my support in life, may God keep you as a steadfast pillar for me: "****Abdel Hamid, Abdel Ouadoud , Abdel Adhim****, and the apple of my eye* ***Abdel Alim*** *and* ***Jinan*** *" .*

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*To my colleague with whom I never regretted sharing this achievement and working with, I am very grateful: "****Ibtihal****".*

To my companions in hardships and studies, " ***Ihssan, Hadjer*** *"*

Ferdaous Bahi

Dedication

"I said 'I will achieve it' and I did.
The journey was not short, nor was it meant to be.
The dream was not near, nor was the path lined with ease.
But I did it and I achieved it.
"Thanks, and praise be to Allah, with love and gratitude, who by His grace, I stand today looking at a long-awaited dream that has now become a reality I am proud of.
*To my pure angel and my strength after God, my first and eternal supporter, my dear mother" **YAHIA SOUAD**" I dedicate this achievement to you. Without your sacrifices, it would not have existed.*
*To the one who has supported me and continues to support me unconditionally, giving without expecting anything in return, to the man who taught me determination and perseverance, and who is a source of hope and ambition, my dear father "**REZAZGA NASEREDDINE**"*
*"To the one who extended his hand tirelessly during my times of weakness, my dear brother, "**REZAZGA AHMED YASSIN**"*
*"To the one who believed in my abilities and is the safety of my "days, my dear sister, **REZAZGA IKBAL**"*
*"To the one who reminds me of my strength and stands behind me like my shadow, my dear sister" **REZAZGA ILHAM**"*
*To my partner in this achievement "**FERDAOUS**"*
To all my big family and to my all friends
At the end I dedicate it to the people who have contributed from near or far to the development of this work.

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Abstract

The world is grappling with rising levels of pollution, particularly organic pollution stemming from industrial and agricultural activities. These pollutants pose a significant threat to the environment and public health, prompting scientists to seek effective solutions for their removal.

This research aims to contribute to understanding the effectiveness of photocatalytic oxidation using specific metal oxides, titanium dioxide (TiO_2) and manganese dioxide (MnO_2), in treating organic pollutants. The study focused on the degradation of methylene blue, a common environmental pollutant, using UV-Vis spectrophotometry.

The results demonstrated the remarkable superiority of TiO_2 performance in neutral media, successfully degrading 49.64% of the pollutant within an hour of irradiation. In comparison, MnO_2 exhibited lower efficiency under the same conditions, achieving a 46.3% degradation rate after one hour and 30 minutes. The optimal concentrations leading to the highest reaction rates in both cases were determined to be 8 ppm for the pollutant. The kinetic model followed a pseudo-first-order rate in both cases.

Key words: pollution , photocatalytic , metal oxides , methylene blue , degradation

Résumé

Le monde est aux prises avec des niveaux croissants de pollution, en particulier la pollution organique provenant des activités industrielles et agricoles. Ces polluants constituent une menace importante pour l'environnement et la santé publique, incitant les scientifiques à rechercher des solutions efficaces pour leur élimination.

Cette recherche vise à contribuer à la compréhension de l'efficacité de l'oxydation photocatalytique utilisant des oxydes métalliques spécifiques, le dioxyde de titane (TiO_2) et le dioxyde de manganèse (MnO_2), dans le traitement des polluants organiques. L'étude s'est concentrée sur la dégradation du bleu de méthylène, un polluant environnemental courant, en utilisant la spectrophotométrie UV-Vis.

Les résultats ont démontré la supériorité remarquable des performances du TiO_2 en milieu neutre, dégradant avec succès 49,64% du polluant en une heure d'irradiation. En comparaison, le MnO_2 a présenté une efficacité moindre dans les mêmes conditions, atteignant un taux de dégradation de 46,3% après une heure et trente minutes. Les concentrations optimales conduisant aux vitesses de réaction les plus élevées dans les deux cas ont été déterminées à 8 ppm pour le polluant. Le modèle cinétique a suivi une loi pseudo-unimoléculaire dans les deux cas.

Mots-clés : pollution, photocatalytique, oxydes métalliques, bleu de méthylène, dégradation

ملخص

يُعاني العالم من تزايد مستويات التلوث، خاصةً التلوث العضوي الناجم عن الأنشطة الصناعية والزراعية. تُشكل هذه الملوثات خطرًا كبيرًا على البيئة والصحة العامة، مما يدفع العلماء إلى البحث عن حلول فعّالة للتخلص منها.

يسعى هذا البحث إلى المساهمة في فهم فاعلية الحفز الضوئي الكيميائي لأكاسيد معدنية محددة، وهي أكسيد التيتانيوم (TiO_2) وأكسيد المنغنيز الرباعي (MnO_2)، في معالجة الملوثات العضوية. ركز البحث على تفكيك مركب أزرق الميثيلين، وهو ملوث شائع للبيئة، باستخدام تقنية التحليل الطيفي بمطيافية المرئي وفوق البنفسجي.

أظهرت النتائج تفوقًا ملحوظًا لأداء TiO_2 في الوسط المتعادل، حيث نجح في تفكيك 49.64% من الملوث خلال ساعة واحدة من التشعيع. بالمقارنة، أظهر MnO_2 فاعلية أقل في نفس الوسط، حيث حقق نسبة تفكيك 46.3% بعد ساعة و 30 دقيقة. وتم تحديد التراكيز المثالية التي أدت إلى أقصى سرعة تفاعل في الحالتين، حيث كانت 8ppm للملوث و النموذج حركي شبه الرتبة الاولى في الحالتين.

الكلمات الدالة : التلوث ,الحفز الضوئي ,الاكاسيد المعدنية ,ازرق ميثيلين , تفكيك

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Chapter I: Chemistry of colors and dyes

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List of Abbreviations

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BBD	Box-Behnken design
C	speed of light in a vacuum
$C_{16}H_{18}N_3S_l$	bis(Dimethylamino)-phenothiazin-5-ium-3,7 chloride
D_e	Degradation capacity at equilibrium
D_t	Degradation capacity at time
E	energy
HCl	Hydrochloric acid
HOMO	Highest occupied molecular orbital
h	Planck`s constant
K1	Pseudo-first-order rate constant
K2	Pseudo-second-order rate constant
LED	light-emitting diode
MB	Methylene blue
MAO	Monoamine oxidase
MnO_2	Manganese dioxide
N	Avogadro`s number
NaOH	Sodium hydroxide
$-NO_2$	Nitrogen dioxide
-N=O	Nitroso
-N=N	Azo
OH	hydroxyl
pH	potential of hydrogen
RSM	Response Surface Methodology
t	time
TiO_2	Titanium dioxide
UV	Ultraviolet
v	radiation frequency
λ	wavelength
λ_{max}	Maximum wavelength of absorption

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index

Chapter II: Photochemistry

Chapter III: Devices and techniques

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GENERAL INTRODUCTION

General introduction

Pollution is one of the major problems facing humans and the environment, especially after technological advancements accompanying contemporary life. Pollution occurs in various forms, whether it's air, water, or soil pollution, due to the presence of harmful organic and inorganic substances or due to imbalances in certain essential environmental components compared to their natural proportions. This occurs as a result of human intervention or due to some natural phenomena.

Water pollution is considered one of the most significant pollution problems due to the crucial role water plays in daily life. Water is the essence of life for all living creatures on earth and plants, as well as being an essential element in industry. Various industries require vast amounts of water that differ in terms of quality and purity levels to meet specific industrial considerations and specifications.

Water pollution takes on various forms, including poisoning by organic and inorganic waste, pesticides, or detergents. It also includes pollution caused by oil spills or by various industries that are too numerous to list here.

In this research, we will present a comparison between the photocatalytic activity of some metal oxides, such as titanium dioxide and manganese (II) oxide, in removing an organic pollutant in an aqueous medium. The test material in this case is **methylene blue**, which is a dye in powder form. When dissolved in water, it gives a blue color with a maximum absorbance at a maximum wavelength of 664 nanometers.

In this study, we employed photocatalytic degradation to partially or completely remove the organic pollutant, methylene blue, in an aqueous medium.

We used the Response Surface Methodology(RSM) to enable the study of multiple important variables simultaneously and to obtain optimal conditions for improving degradation. In our study we focused on investigating three variables that influence the degradation process (mass, time, pH). It is appropriate to summarize all of this and appreciate it in this memorandum. The process was conducted in stages divided into four chapter, which included the following titles:

Theoretical part:

The first chapter: chemistry colorants and dyes encompass their classification, types, toxicity levels, removal methods, and we also provided general information about the methylene blue, including its definition, physical and chemical properties, and the most important methods contributing to its removal from aqueous environment.

The Second chapter: theoretical principles of photochemistry and their sources, types of catalytic photodecomposition, and finally, the definition of some metal oxides and their physical and chemical properties (titanium dioxide, manganese dioxide), and their effectiveness in removing organic pollutants.

Experimental part:

The third chapter: the materials, equipment, and techniques used in all steps of the work.

The fourth chapter: Analysis, discussion, and interpretation of the obtained results.

Theoretical Part

Chapter I:
Chemistry of colors and dyes

I.1. Chemistry of colors and dyes

Color has been a constant element in human experience, from prehistoric cave paintings to the modern world, Until the late 1800s, all colors came from natural sources like plants, trees, and insects. However, only a few were practical due to their impermanence. The invention of synthetic dyes revolutionized the field. Today, there are over 7,000 synthetic dyes compared to the limited options from nature.

The vast majority of the natural dyes used prior to the nineteenth century have been replaced by synthetic dyes discovered since then. The early advances made in organic chemistry were largely responsible for this remarkable revolution and for many years organic chemistry and dyestuffs chemistry were inextricably linked.

Dyes are colored chemical substances with a fixed color that can color other materials (such as fabrics or fibers in general) so that the color adheres to the other material and does not fade with washing or rubbing.

There is a difference between dyes and colored materials. Many colored materials exist, but their color does not adhere to another material and therefore are not considered dyes.

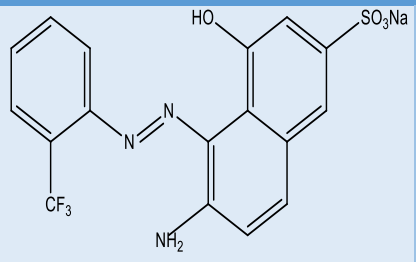
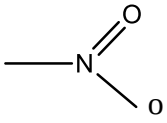
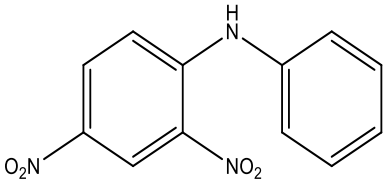
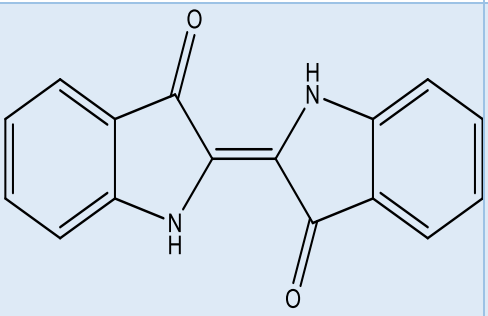
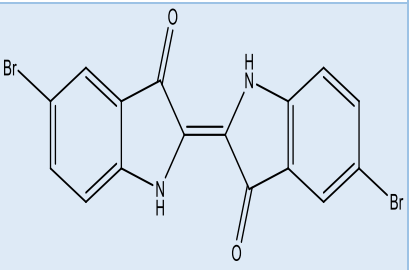
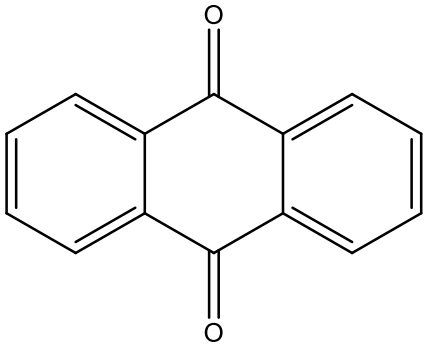
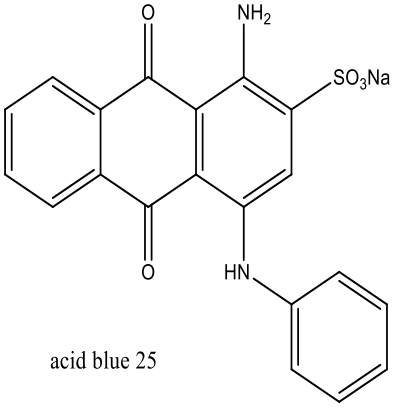
From a chemical point of view, the scientist Witt proposed the chromophore theory. This theory states that for a compound to be a dye, its molecule must contain special units or groups called chromophores.

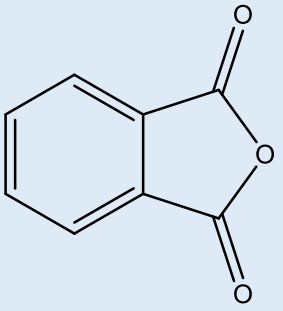
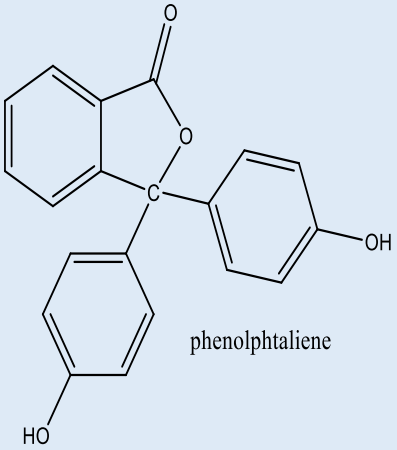
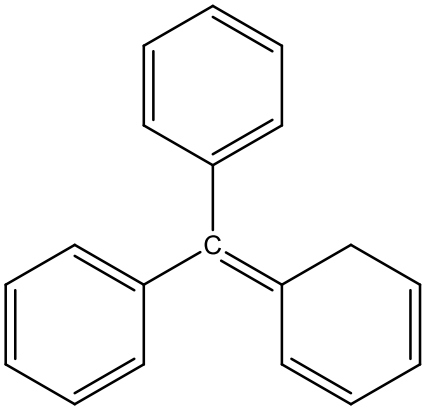
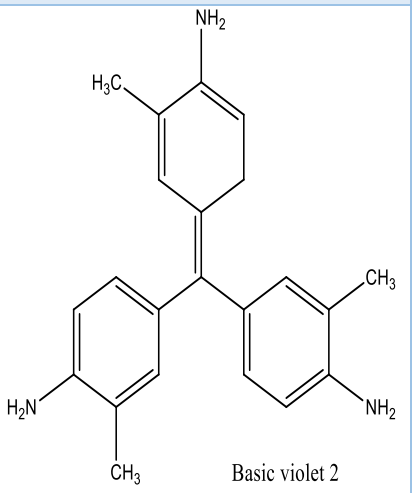
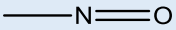
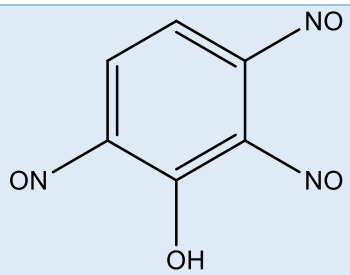
Chromophores are color carriers. They are groups or clusters of atoms that cause the compound to be colored. These groups are characterized by unsaturation (containing double bonds). Some of the most famous chromophores include the nitro ($-NO_2$), nitroso (-N=O), azo (-N=N), and carbonyl groups.[1]

I.2. Classification of dyes

Dyes may be classified by their use or by their chemical structure.

A. **Classification according to their structure** :[2]

class	Chromophores	Exemple
Azo dyes	−N=N−	 acid red 337
Nitro dyes		 Dispers yellow 14
Indigo dyes		 C.I. Vat blue 35
Anthraquinone dyes		 acid blue 25

Phthalien dyes		 phenolphtaliene
Triphenyl methyl dyes		 Basic violet 2
Nitrated dyes		 fast green O

B. **Classification according to their use** :[3]

a) Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. And Most synthetic food colors fall in this category.

b) Basic dyes are water - soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. They are also used in the coloration of paper.
c) Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.
d) Food dyes can be direct mordant and vat dyes, and their use is strictly controlled by legislation. Some naturally - occurring dyes are also used.

I.3. The Uses of Dyes

The dye industry is a large economic market because many industrial products can be colored. The most important of these are:[4]

a) Food industry (food coloring)
b) Plastics and paint industries
c) Textile industry
d) Cosmetics industry (hair dyes)
e) Textile dyes for clothing, decoration, construction, and medical use
f) Printing (ink and paper)
g) Pharmaceutical industry (dyes and preservatives)

I.4. The Toxicity of Dyes

Looking at the massive use of dyes in the food industries, especially in the confectionery industry, this has caused problems related to human health, and the examples below illustrate that:

In 1959, Look showed the existence of side effects on human health when exaggerating chemical additives, and after a few years, in 1972, Juhlin found cases of skin rashes in the presence of tartrazine.

Erythrosine is the dye widely used to color all types of confectionery. CLEMENT showed that this compound has caused serious cases of sensitivity for people who consume it greatly.

OB Yellow and AB Yellow are used to color butter and ghee, and they have a high degree of toxicity, where their toxicity appears through some symptoms such as inflammation of the digestive system, low growth, and increased total weight.[5]

I.5. Colorant Removal Methods

Removal methods include laboratory processes :[6]

a) Physical and chemical processes: Adsorption , Membrane ,separation ,Solid-liquid separation (Sedimentation, Coagulation, Flocculation ,Deposition)
b) Chemical methods: Ion exchange , Oxidation with oxygen ,Ozonation…
c) Biological methods: Aerobic , Anaerobic

I.6. Methylene Blue

Methylene blue dye is a heterocyclic aromatic chemical compound with a planar structure.It has a molceular weight and chemical formula of 319.85 g/mol and $C_{16}H_{18}N_3S_1Cl^-$ .It is a solid, powdered material with a dark green color and no odor.[7]

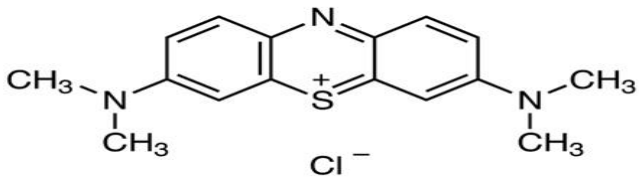


Figure (I.1): Molecular structure of methylene blue

I.6.1. Physico-chemical properties of methylene blue[7]

Entery	Parameters	Values/Names
1.	Maximum wavelength of absorption (λ_{max})	664 nm
2.	Another name	Swiss blue
3.	Ionization	Basic
4.	Degree of solubility	3.55%
5.	Color index name	Basic blue 9
6.	Color index number	52015
7.	Aqueous pH	Strongly acidic between pH 2.0–3.5

I.6.2. Methylene Blue Applications

Methylene blue is a versatile dye with numerous applications.

a) **Medical:**

Early antimalarial drug.

Treatment for methemoglobinemia (blood disorder).

Treats hypoxia (low oxygen levels) and hyperdynamic circulation in liver cirrhosis.

Reduces mortality in vasoplegic (hypotensive) patients after transplant surgery.

b) **Industrial:**

Dyes fabrics, paper, and leather.

c) **Food:**

Indirect food additive.

d) **Other:**

Treats fish diseases in aquaculture[7].

I.6.3. Toxicity of methylene blue dye

- Toxic to aquatic life and humans at high concentrations
- Carcinogenic and non-biodegradable
- Improper disposal from industries pollutes water sources
- Health risks include gastrointestinal issues, respiratory problems, and skin irritation
- Can act as a MAO inhibitor, leading to serotonin toxicity if overdosed This compound is prepared by oxidation of 4-aminodimethylaniline in the presence of sodium thiosulfate to give the quinonediiminothiosulfonic acid, reaction with dimethylaniline, oxidation to the indamine, and cyclization to give the thiazine[7]

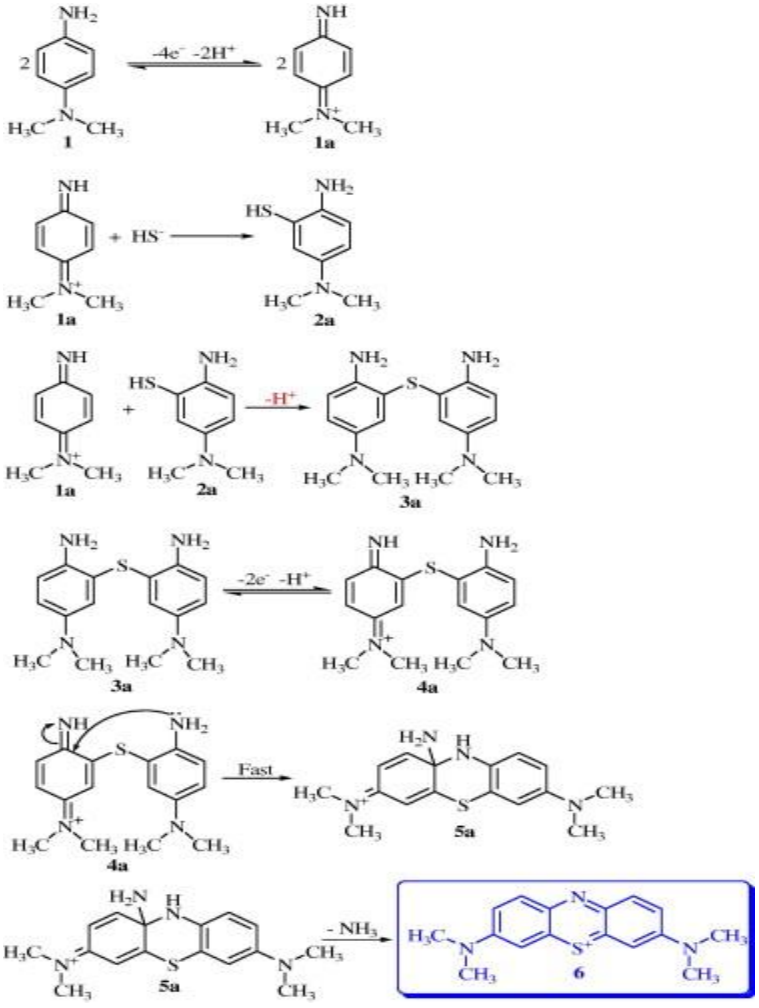


Figure (I.2): Preparation of methylene blue

I.7. Metal Oxides

Metal oxides are crystalline solids that contain a metal cation and an oxide anion. They typically react with water to form bases or with acids to form salts .Since the mid-twentieth century, metal oxides have been extensively employed in the chemical industries, particularly as catalysts for the oxidation of certain substances and also as catalysts for the conversion of certain toxic pollutants into non-toxic materials.

I.7.1.Titanium dioxide (TiO_2)[8]

IUPAC names	Titanium dioxide Titanium(IV) oxide
Chemical formula	TiO2
Molar mass	79.87g/mol
Appearance	White solid
Density	4.23 g/cm
Melting point	1870 °C
Solubility	Insoluble in water

Titanium dioxide (TiO_2) is a versatile n-type semiconductor characterized by a bandgap energy ranging from 3.04 to 3.46 eV, high resistivity at room temperature, high transparency in the visible range, and excellent reflectivity in the infrared region[9]. Among various semiconductors, TiO2 stands out as a prominent candidate for photocatalysis due to its unique combination of optical and electronic properties, chemical stability, abundance, low cost, and non-toxicity.[10]

I.7.2. Manganese dioxide (MnO_2)

IUPAC names	Manganese dioxide Manganese(IV) oxide
Chemical formula	MnO_2
Molar mass	86.9368 g/mol
Appearance	Brown-black solid
Density	5.026 g/cm3
Melting point	535 °C (995 °F; 808 K)
Solubility	Insoluble in water

Moreover, manganese dioxide has good catalytic potential even at low temperature [11] MnO2 has a narrow bandgap energy of 1~2 eV. Thus, it possesses high possibility to be driven by visible light and infrared light for dye degradation[12] . And manganese oxide (MnO_2) is regarded as the most attractive oxide material due to its high pseudocapacitance, low cost, and environmental friendliness [13]

Reference

Reference

[1] H. Zollinger, *Color chemistry: syntheses, properties, and applications of organic dyes and pigments*. John Wiley & Sons, 2003.

[2] P. F. Gordon and P. Gregory, *Organic chemistry in colour*. Springer Science & Business Media, 2012.

[3] T. I. J. U. h. w. r. n. P. Kakhia, "Dyes, colors & pigments," 2015.

[4] A. Boulal and B. J. M. d. M. Mustapha, Université Oran Mohamed Boudiaf, "Etude cinétique de la dégradation d'un colorant par oxydation," 2013.

[5] K. Djebbar and S. Aliouche, "Etude de l'élimination d'un colorant par différentes méthodes photochimiques en milieu aqueux."

[6] N. N. J. M. d. M. Merzoug, Université Mohamed Cherif Massaadia Souk-Ahras, Alger.. P, "Application des tiges de dattes dans l'adsorption de polluants organiques," 2014.

[7] P. O. Oladoye, T. O. Ajiboye, E. O. Omotola, and O. J. J. R. i. E. Oyewola, "Methylene blue dye: Toxicity and potential elimination technology from wastewater," vol. 16, p. 100678, 2022.

[8] A. Piscopo, "Chimie solaire et traitements photocatalytiques des eaux polluées: applications aux traitements sélectifs et exemple d'utilisation de catalyseurs supportés," Université Paul Verlaine-Metz, 2002.

[10] M. Fujishima *et al.*, "Isolation and structural analysis in vivo of newly synthesized fructooligosaccharides in onion bulbs tissues (Allium cepa L.) during storage," vol. 2009, 2009.

[11] J. Zhang, L. Wang, Z. Wu, H. Wang, B. Zhang, and F. S. J. A. J. Xiao, "Mesoporous Co-Al oxide nanosheets as highly efficient catalysts for CO oxidation," vol. 66, no. 5, p. e16923, 2020.

[12] S.-L. Chiam, S.-Y. Pung, F.-Y. J. E. S. Yeoh, and P. Research, "Recent developments in MnO2-based photocatalysts for organic dye removal: a review," vol. 27, no. 6, pp. 5759-5778, 2020.

[13] X. Dong *et al.*, "Synthesis of a MnO2–graphene foam hybrid with controlled MnO2 particle shape and its use as a supercapacitor electrode," vol. 50, no. 13, pp. 4865-4870, 2012.

Arabic Reference

[9] ص. نجاح و س. عاشور, "دراسة البنى النانومترية لأكسيد التيتانيوم".

[14] الزهراء اسماعيل حسن " التخلص من ملوثات المياه بواسطة ظاهرة الامتزاز" مذكرة بكالوريوس - جامعة القادسية - بغداد - العراق - كلية العلوم - قسم علوم الكيمياء 8 ص 2017 / هـ 1438

Chapter II:
Photochemistry

II. Introduction

Photochemistry and photolysis are two important branches of chemistry that deal with the interaction of light with matter and the chemical reactions that result from these interactions

II.1. Photochemistry

Photochemistry is the study of chemical changes caused by the impact of light on molecules. There are two laws that govern photochemical reactions. The first law is" **The Grotthuss-Draper** "this law states that a chemical substance must absorb light. In order for photochemical reaction to occur. In other words, no photochemical reaction occurs for molecules that do not absorb light at a specific frequency. The second law is" **The Einstein-stark law'',** which states that each photon of light absorbed by a chemical system activates only one molecule in any photochemical reaction. This law is also known as the law of equivalence and was announced by **Albert Einstein** at the time when the quantum theory of light was established by the German physicist **Max-Planck** and the French physicist **Louis Broglie.** **[1]**

II.2. Fundamentals of photochemistry

Light has a wave-like nature, allowing it to be considered electromagnetic waves. It also possesses a particle-like nature, consisting of elementary units called photons that travel at the speed of light and can even move through a vacuum, unlike waves that require a material medium to propagate through. Waves exhibit a pattern of minima and maxima in their curves. Wavelength is defined as the distance between two consecutive values.

The relationship describes light by energy:

$$\mathrm{E}= h\nu = h\ c/\lambda \quad (\frac{j}{photon}) \dots\dots\dots\dots\dots (\mathrm{II}.1)$$

Radiation can be broadly classified as follows:[5]

- Lambda radiation γ $(0{,}005 - 0{,}025nm)$
- X radiation (0,025-10nm)
- Ultraviolet radiation UV (10-400nm)

- Visible radiation (400-800nm)
- Infrared radiation (800-3000nm)

II.3. Photochemical methods

II.3.1. UV light assisted advanced oxidation process

With the assistance of UV light, highly reactive radicals such as hydroxyl radicals and sulphates are generated which in-turn attack the methylene bleu dyes leading to the formation of non-toxic or less toxic products.[2] Ordinary UV light is limited in the acidic and natural media for the removal of methylene bleu dyes. [3]Hence, UV light has been used to assist other methods/reagents.

The use of hydrogen peroxide with UV light has been reported for the degradation of methylene bleu. And plasma technology ……and others.

II.3.2. Catalyst assisted advanced oxidation process

The mechanism of photocatalytic degradation of organic pollutants has been widely reported in the literatures.[4] [5] [6] The summary from these literatures is summarized in **fig(II.1).** Briefly, solar light is absorbed by the photocatalysts to generate pairs of electrons and holes when the light possesses enough photon energy which is more than or equal to the band gap energy of the photocatalyst. The generated electrons-holes pairs migrate to the surface of the photocatalyst to undergo a redox reaction.[7] [8]

However, a lot of these holes and electron pairs recombine to dissipate energies in the form of light and heat. The unrecombined electrons are excited to the conduction band of the photocatalyst while the holes in the valance band of the photocatalyst attacks the methylene bleu dye and some of the hole also react with water to generate hydroxyl radicals which in-turn strongly oxidize the methylene bleu dye. The excited electrons on the other hand further attack the oxygen to form superoxide anion radicals which also degrade the methylene bleu dye in the presence of photocatalyst and light into carbon dioxide, water and other less toxic or non-toxic substances. The efficiency of the photocatalyst depends on the light intensity and the type of photocatalyst used. [9]

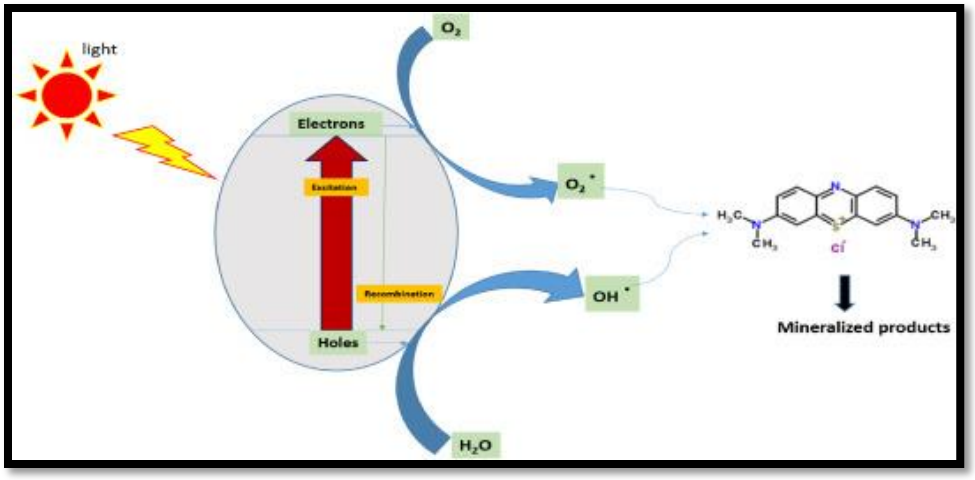


Figure (II.1): Mechanism of photocatalytic degradation of methylene bleu.[14]

II.4. Sources of light radiation

During the mid-19th century, some inventors attempted to produce light from electricity. Many pioneers succeeded in developing incandescent light bulbs. These lamps worked on batteries, but they quickly burned out.

The widespread use of electric light did not only require the availability of a light bulb, but also a cheap way to distribute electricity to the owners of the bulbs. Therefore, the American inventor **Thomas Edison** developed such a method and thus became the discover of electric light. In 1879, **Edison** invented his incandescent light bulb, and during the early years of the 20th century, **Edison** developed the first power plant to generate and distribute electricity. This plant was located on pearl street in New York city and began operating in 1882.

After that, in the early twentieth century, engineers began experimenting with developing electric lighting using gas discharge lamps. Their work led to the development of fluorescent lamps and mercury vapor lamps in the 1930s.

Electric lighting was discovered in 1936. Liquid crystal displays and light-emitting diodes were developed as a result of research using semiconductors in the 1960s. In the 1970 researchers were able to develop light sources.[13]

The following are some types of lighting lamps in detail:

1. **Incandescent lamp**

Incandescent lamps are the most common sources of electric light. An incandescent lamp consists of a metal filament inside a glass bulb that has been evacuated of air. The base of the lamp and the filament are either in a spiral or nail shape. The amount of light emitted from an incandescent lamp depends on the amount of electricity it consumes .[13]

2. **Gas discharge lamps**

Gas discharge lamps produce light by passing electricity through a gas under pressure, instead of filament incandescence. Gas discharge lamp include neon lamps, low-pressure and high-pressure sodium lamps, mercury vapor lamps, and metal halide lamps .[13]

3. **Fluorescent lamp**

A fluorescent lamp consists of a glass tube containing a small amount of mercury vapor and another inert gas under low pressure, often argon gas. A layer of phosphor material is applied to the inner surface of the tube, and at each and of the tube is an electrode made of tungsten wire coated with a chemical called rare earth oxides.

When the lamp is turned on, the current flows through the tungsten filament, causing the rare earth oxides to emit electrons, these electrons collide with argon atoms and ionize them, causing a current to flow through the gas from one electrode to another, forming an arc. When an electron in the arc collides with a mercury atom, it raises the energy level of some returns to its normal state, it emits invisible ultraviolet radiation, which is absorbed by the phosphor material coating the inner surface of the tube, producing visible light that depends on the color of the phosphor material used.[13]

4. **Laser lamp**

It is a type of electromagnetic radiation with a single wavelength, where its photons have equal frequencies and are in the same phase, which gives these rays high energy and a very small angle of refraction.[1]

5. **Mercury vapor lamps**

In this type of lamps, the discharge between the electrodes causes the excitation of mercury atoms, which emit radiation when they return to their ground state.

There are actually three main types of mercury vapor lamps: low pressure, medium pressure, and high pressure.[1]

a) **Low-pressure mercury lamp**

It emits primarily at a wavelength of 254 nm (more than 80% of the radiant energy). At 184,9 nm, the radiant ranges between 20% and 10% of the total luminous flux, but it is quickly absorbed by oxygen, water, or a transparent material (quartz) that forms the lamp envelope.[1]

b) **High-pressure and medium-pressure mercury lamp**

High-pressure mercury lamp, which utilizes its maximum emission at the resonance line of 365nm, operate similarly to medium-pressure lamps but under much higher temperature conditions than low-pressure lamps, hence the need for a cooling system.[1]

II.5. Light absorption

The interaction between electromagnetic radiation and a molecule can lead to the absorption of a photon by the molecule. This occurs due to the transition of an electron from an occupied orbital to an excited state. This state is only observed when the energy of the absorbed photon is equal to the energy difference between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO). There are two main cases where a molecule can be electromagnetically excited:

$$M= 2S+1 \qquad \text{..... (II.2)}$$

In the excited state where electrons spin in pairs, the total spin is equal to zero, i.e. S=0, and therefore M=1. This state is called a singlet state (Si). If the two electrons have the same spin, the total spin in in this case is equal to one, S=1, i.e. M=3. This state is called a triplet state (T).

The triplet state (T) has lower energy than the singlet state (S). The energy value carried by a photon is expressed by Planck`s relation:

$$E = h\,c/\lambda = h\nu \quad (j/photon) \quad \ldots\ldots\ldots\ldots\ldots (II.3)$$

h: Planck`s constant ($6{,}626\times10^{-34}$) (j/s)

C: speed of light in a vacuum (3×10^{8}) (m/s)

$\boldsymbol{\lambda}$:wavelength (m)

$\boldsymbol{\nu}$:radiation frequency (S^{-1})

The energy absorbed by a molecule is the same as the energy given in Planck's relation: which is the energy of a single photon.

$$A + h\nu \xrightarrow{E = h\nu} A^{*} \ldots\ldots\ldots\ldots\ldots \text{(II.4)}$$

(ground state) (excited state)

The energy of one mole of photon is given by the following equation:

$$E = N\,h\,c/\lambda \ (\frac{j}{mol}) \ldots\ldots\ldots\ldots\ldots\ldots \text{(II.5)}$$

N: Avogadro`s number ($6{,}023\times10^{23}$)

This quantity is called (Einstein unit) and it is a value related to the wavelength of the absorbed light. The equation becomes:

$$1\ \text{Einstein} = 1{,}2\times10^{5} \ /\lambda \ (J) \ldots\ldots\ldots (II.6)$$

The photon flux (I_0) is defined as the number of emitted photons (n) per unit time (t) during the irradiation period.

$$I_0 = n/t \ (\text{Einstien}.\text{sec}^{-1}) \quad \ldots\ldots\ldots (II.7)$$

(1 Einstein =Energy of 1 mol of photons = 1 Energy of N photons)

When the interaction medium receives radiation, the incident flux (I_0) is divided into three parts:

- The absorbed part (I_a) by the material.
- The reflected part (I_r).
- The transmitted part (I_t).

$I_0 = I_a + I_r + I_t$ ……... (II.8)

The ratio of the absorbed flux to the incident flux is called the absorption coefficient ε_0:

$$\varepsilon 0 = Ia/Io$$

Both the reflection coefficient (R) and the transmission coefficient (T) are defined by the following relation: $R = I_r/I_0$, $T = I_t/I_0$

Lambert-Beer`s law allows us to obtain a relationship between absorbance and concentration. This law states that there is a logarithmic relationship between the transmittance of light (T) through a material and the product of the molar absorption coefficient of the material in units of (L/mol.cm), the distance travelled by the light through the material (L) in units of (cm), and the concentration absorbing substance (c) in units of (mol/l).[1]

$$A = -\text{Log}_{10}(I/I_0) = -\text{Log}_{10}(T) \text{ ……... (II.9)}$$

$$T = I/I_0 = 10^{-\varepsilon LC} = 10^{-A} \text{ ……... (II.10)}$$

The relationship of absorbance:

$$A = \varepsilon LC \text{…… (II.11)}$$

From the above relationship of absorbance, it is shown that there is a direct relationship between absorbance and concentration. Therefore, it is possible to determine the concentration and specify its value by knowing the value of absorbance.

The range of wavelength commonly used in photochemistry is between (200 and 700nm). The energy is (10^{-18} and 3×10^{-17} J/photon), which means that the photon energy is between (600 and 800 kJ/mol).

II.6. Photodegradation of pollutants

Traditional treatment methods such as membrane filtration, chemical coagulation, and biological treatment have been shown to be unable to completely remove some pollutants from water, or the results have not been satisfactory. Therefore, photolysis (advanced photocatalytic oxidation) technology has been used to eliminate these pollutants.

There are many methods for the analysis of organic compounds and pollutants, including ultraviolet radiation, either directly or in some cases in conjunction with hydrogen peroxide and semiconductors. In the latter two cases, this type of combination is called advanced oxidation processes, which are based primarily on oxidation reactions that lead to the production of a very strong oxidant such as the hydroxyl radical OH. It is important to distinguish between advanced oxidation in homogeneous media, which produces more toxic and harmful products than the pollutants themselves, while advanced oxidation in heterogeneous media uses semiconductors. Many published studies have shown that advanced oxidation using semiconductors and UV radiation has a very high efficiency in removing color completely, and also partially removes the decomposition products of these dyes. Thus, we can avoid the problem of dye degradation by using semiconductors. In this process, hydroxyl radicals are generated when the catalyst is irradiated, and in the presence of water and air, this high efficiency and the accompanying oxygen are able to complete the complete degradation of organic pollutants and convert them into carbon dioxide, water and some other non-toxic compounds.[14]

Traditional water treatment methods are ineffective in removing contaminants present in water due to:

II.6.1. Biological degradation: some contaminants are not easily biodegradable, leading to their accumulation in the environment.

II.6.2. Precipitation of organic pollutants or their adsorption on activated carbon or other adsorbent material:

- These methods may not be effective in removing all pollutants.
- Disposal of sludge or adsorbents can be difficult and expensive.

Therefore, photolysis technology has been chosen as an effective alternative to traditional methods.

Photolysis technology has several advantages, including:

- High efficiency in removing various organic pollutants, such as dyes, pesticides, and aromatic compounds
- High speed of treatment process.
- Environmentally friendly technology, as it does not produce any harmful residues.

Photolysis technology relies on:

- Generation of highly effective oxidizing agents, the most important of which are hydroxyl radicals (OH).
- Hydroxyl radicals oxidize organic pollutants of different types at high speed.

Therefore, photolysis technology is a promising solution for the treatment of polluted water.

There are two types of photolysis: **direct photochemical dissociation** and **photocatalytic chemical dissociation**. [1]

II.7. Direct photochemical Dissociation

Pollutants can be decomposed by direct photoexcitation. To achieve this, pollutants must have a high light adsorption capacity to be excited and react with dissolved oxygen in water before being converted to by-products.

When a molecule is exposed to light within its adsorption spectrum, various electronic transitions occur between bonding, no-bonding, and anti-bonding molecular orbitals. [15]

II.8. Photocatalytic Chemical Dissociation

Photocatalytic research began in the early 1970s with the proposal of a technique using ultraviolet (UV) light and titanium dioxide (TiO_2) for the removal of pollutants in water treatment. Numerous studies have demonstrated the effectiveness of this method on a wide range of organic compounds, including saturated and unsaturated hydrocarbons, oxygenated compounds, pesticides, dyes, fatty acids, and aromatic derivatives. The method is carried out in the presence of a catalyst and there are two types of these photocatalytic reactions:[10]

- Homogeneous photocatalytic reactions.
- Heterogeneous photocatalytic reactions.

II.8.1. Homogeneous photocatalytic Dissociation

This method is carried out by forming unstable intermediates between the catalyst and the reactants, which then decompose and the catalyst is recovered again. In general, these reactions are of two types: (acid/base) and (reduction/oxidation).

Homogeneous photocatalytic dissociation is a promising method for the removal of pollutants from water and air.

The use of homogeneous photocatalytic dissociation for the degradation of organic pollutants has been extensively studied.

II.8.2. Heterogeneous photocatalytic Dissociation

Photocatalytic is a process that relies on a substance to increase the rate of conversion of reactants without being affected or depleted. This substance is known as s **"catalyst"**. It increases the reaction rate by lowering the activation energy required for the reaction.

therefore, photocatalysis is a reaction in which light is used as an activator for the substance that will increase the rate of the chemical reaction without any effect on the reaction. itself. As shown in **figure (II.2).[11]**

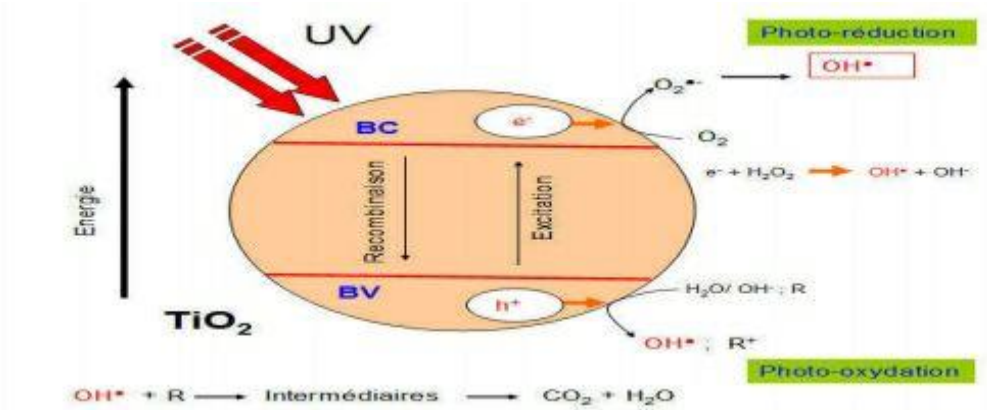


Figure (II.2): Mechanism of photochemical catalysis.[14]

Semiconductors have been chosen as photocatalysts due to their unique properties that make them suitable for driving light-induced chemical reactions. These materials possess a characteristic energy gap between their valence band (VB) and conduction band (CB). Upon exposure to light with energy equal to or greater than this gap, electrons from the VB are excited into the CB, generating electron-hole pairs.

semiconductors serve as excellent photocatalysts due to their unique ability to absorb light energy, generate electron-hole pairs, and facilitate redox reactions. Their photocatalytic properties are governed by their band structure, energy gap, and the presence of impurities or defects. Understanding the fundamental principles of semiconductor physics and band gap theory is essential for designing and optimizing photocatalytic materials for various applications.

II.9. Degradation kinetics

Degradation kinetics involves studying the rate of degradation of materials over time [12]It includes analyzing processes like thermal decomposition, photolysis, and hydrolysis that lead to the breakdown of substances[13]

II.9.1. Pseudo-First-Order Kinetic Model: Lagergren Model

The Lagergren pseudo-first-order kinetic model describes the degradation process using the following equation:

$$dDt/dt = k1(D_e - D_t)…….(II.12)$$

where:

k1: Pseudo-first-order rate constant (min $^{-1}$)

D_e: Degradation capacity at equilibrium (mg/g)

D_t: Degradation capacity at time t (mg/g)

By taking the natural logarithm of both sides of Equation (II.12) and applying the initial conditions $D_t = 0$ at $t = 0$ and $D_t - D_e$ at $t = t$ the equation becomes:

$$Ln\ (D_e - D_t) = -k1t + ln(D_e) \ldots\ldots\ldots\ldots (II.13)$$

II.9.2. Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model describes the degradation process using the following equation:

$$dD\_t/dt = k_2\ (D_e - D_t)^2 \ldots\ldots\ldots\ldots (II.14)$$

where:

k_2: Pseudo-second-order rate constant (g/mg. min)

D_e: Degradation capacity at equilibrium (mg/g)

D_t: Degradation capacity at time t (mg/g)

By integrating Equation (II.14) and applying the initial conditions $D_t = 0$ at $t = 0$ and $D_t - D_e$ at $t = t$ the equation becomes:

$$\frac{t}{D_t} = \frac{1}{k_2 De^2} + \frac{1}{De} t \ldots\ldots\ldots (II.15)$$

Reference

Reference

[1] K. Djebbar and S. Aliouche, "Etude de l'élimination d'un colorant par différentes méthodes photochimiques en milieu aqueux".

[2] D. Wen, W. Li, J. Lv, Z. Qiang, and M. J. J. o. h. m. Li, "Methylene blue degradation by the VUV/UV/persulfate process: Effect of pH on the roles of photolysis and oxidation," vol. 391, p. 121855, 2020.

[3] T. Soltani and M. H. J. J. o. M. C. A. C. Entezari, "Photolysis and photocatalysis of methylene blue by ferrite bismuth nanoparticles under sunlight irradiation," vol. 37 ,7pp. 197-203, 2013.

[4] T. O. Ajiboye, O. A. Oyewo, D. C. J. S. Onwudiwe, and Interfaces, "The performance of bismuth-based compounds in photocatalytic applications," vol. 23, p. 100927, 2021.

[5] T. O. Ajiboye, O. A. Oyewo, and D. C. J. E. C. L. Onwudiwe, "Photocatalytic removal of parabens and halogenated products in wastewater: a review," vol. 19, pp. 3789-3819, 2021.

[6] T. O. Ajiboye, A. T. Kuvarega, and D. C. J. A. S. Onwudiwe, "Recent strategies for environmental remediation of organochlorine pesticides," vol. 10, no. 18, p. 6286, 2020.

[7] T. O. Ajiboye, O. A. Oyewo, and D. C. J. F. Onwudiwe, "Adsorption and photocatalytic removal of Rhodamine B from wastewater using carbon-based materials," vol. 29, p. 100277, 2021.

[8] Y. Chen, J. Yang, L. Zeng, M. J. C. R. i. E. S. Zhu, and Technology, "Recent progress on the removal of antibiotic pollutants using photocatalytic oxidation process," vol. 52, no. 8, pp. 1401-1448, 2022.

[9] M. Humayun, C. Wang, and W. J. S. M. Luo, "Recent progress in the synthesis and applications of composite photocatalysts: a critical review," vol. 6, no. 2, p. 2101395, 2022.

[10] G. Kumar, R. K. J. P. S. Dutta, and E. Protection, "Sunlight mediated photo-Fenton degradation of tetracycline antibiotic and methylene blue dye in aqueous medium using FeWO4/Bi2MoO6 nanocomposite," vol. 159, pp. 862-873, 2022.

[11] S. Hmamouchi, A. El Yacoubi, and B. C. J. H. El Idrissi, "Using egg ovalbumin to synthesize pure α-Fe2O3 and cobalt doped α-Fe2O3: structural, morphological, optical and photocatalytic properties," vol. 8, no. 2, 2022.

[12] J. P. Martins *et al.*, "3D printing: Prospects and challenges," pp. 299-379, 2018.

[13] D. Spatz, B. C. ERB, K. White, and D. Young, "Standard operating procedure for using the NAFTA guidance to calculate representative half-life values and characterizing pesticide degradation," 2015.

[14] M. I. Din, R. Khalid, J. Najeeb, and Z. J. J. o. C. P. Hussain, "Fundamentals and photocatalysis of methylene blue dye using various nanocatalytic assemblies-a critical review, vol. 298, p. 126567, 2021.

Arabic Reference

[15] قصى عدنان نعمة "تحضير ودراسة الفعالية الضوئية المحفزة للمكونة النانوية MWCNT/Au-ZnO باستخدام تقنية التفكك الحراري "مذكرة الماجستير في علوم الكيمياء 2005 " جامعة القادسية - كلية التربية قسم الكيمياء 1438 هـ /2017 م ص 10.9.8.7

[16] بشرى رحمة ايمام " مصابيح الانارة واستخداماتها في المنازل والمصانع " جامعة ام درمان الاسلامية - السودان - كلية العلوم الهندسية - قسم الهندسة الكهربائية والالكترونية 1.2.3.4.6 ص

Experimental Part

Chapter III:
Devices and techniques

III.1. Materials, Tools, and Equipment used

III.1.1Materials used

- Methylene blue dye(1000mg/l).
- Distilled water.
- Titanium dioxide **(TiO_2)**.
- Manganese(IV) oxide **(MnO_2)**.
- NaOH (0,01M).
- HCL (0,01M).

III.1.2Tools used

- Glass pipette 2 ml.
- Volumetric flask 250 ml.
- Beaker 250 ml.
- Test tubes.
- Watch glass.
- Spatula.
- Magnetic bar.

III.1.3.Equipment used

In this work, we have used a variety of devices, each of which plays a role in meeting different needs. We will explain them below:

1. **Electronic sensitive scale**

Figure (III.1): electronic sensitive scale

2. **Magnetic resonance imaging machine (MRI)**

Figure (III.2): magnetic resonance imaging machine.

3. Instrument pH meter

Figure (III.3): Instrument pH meter.

4. Radiation therapy

In this work, we fabricated a radiation system due to its unavailability at the university. The system consists of a box that we wrapped using aluminium, and we installed two LED light on its surface. The box also has a door to insert the sample to expose it to the maximum possible amount of light.

Figure (III.4):external radiation therapy.

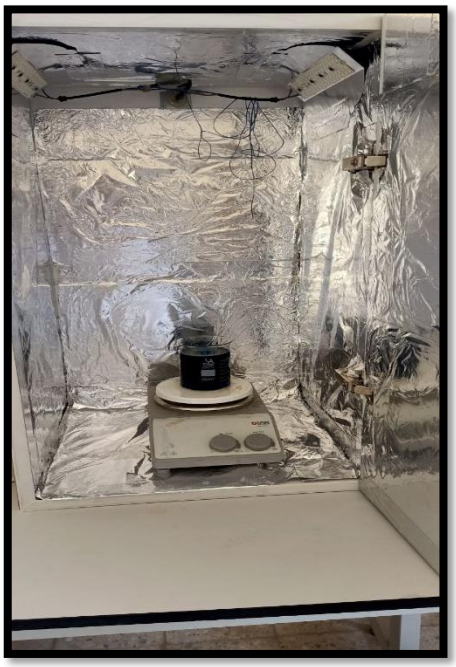


Figure (III.4.1):internal radiation therapy.

4. Centrifuge

Figure (III.5) : centrifuge

5. Ultraviolet-visible (UV-Vis) spectrometer

This is a binary system that uses water as a reference. This device is used to obtain the absorption the absorbance of the samples.

Figure (III.6) : Ultraviolet-visible (UV-Vis) spectrometer

III.2. Preparation of solutions

The chosen dye is **Methylene Blue** with the following chemical formula:

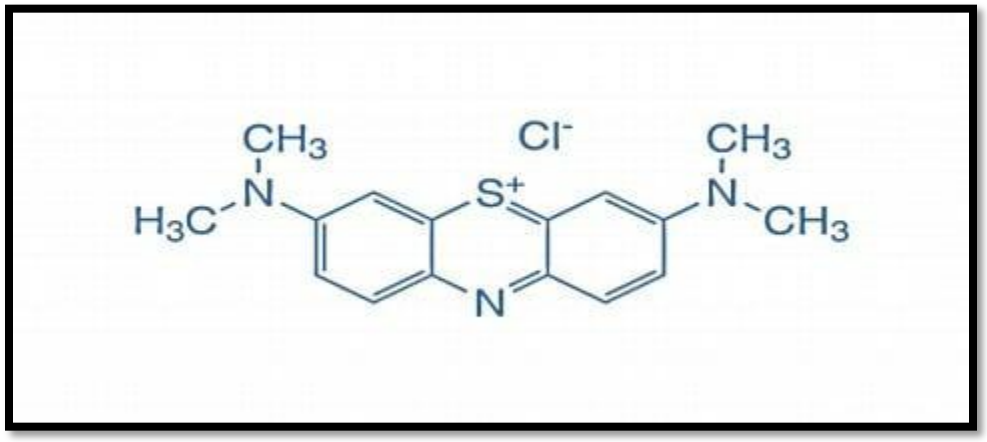


Figure (III.7): The chemical formula of Methylene Blue

III.2.1. Preparation of mother solution

We prepared a solution of methylene blue (MB) with a concentration of 1000 mg/L and a volume of 1000 ml by weighing 1g of methylene blue using an electronic balance, then adding it to a 1000 ml volumetric flask and filling it up with distilled water while stirring to homogenize the solution. Finally, we wrapped the flask in aluminium foil to protect the solution from light exposure.

In the following figure, there is a symbolic representation of the mother solution:

Figure (III.8): Symbolic representation of the mother solution of BM.

To determine the maximum wavelength, the MB solution was passed through a **UV-Visible** device to measure the absorption spectrum in the visible rang (380-750nm).

III.2.2. Determine witness curve

In order to determine witness curve, standard solutions were prepared with deferent concentrations ranging from (5-40mg/L), with a volume of 50ml of each one, based on the dilution law. The absorbance was then measured using a **UV-Visible** spectrophotometer at a wavelength of $\lambda = 664$ nanometers.

We take a specific volume of the mother solution with a concentration of methylene blue (MB) and place it in standard flasks with a capacity of 250ml.

We add distilled water to the flasks, making sure to cover them with aluminium foil, and then place them in test tubes. As shown in the following figure:

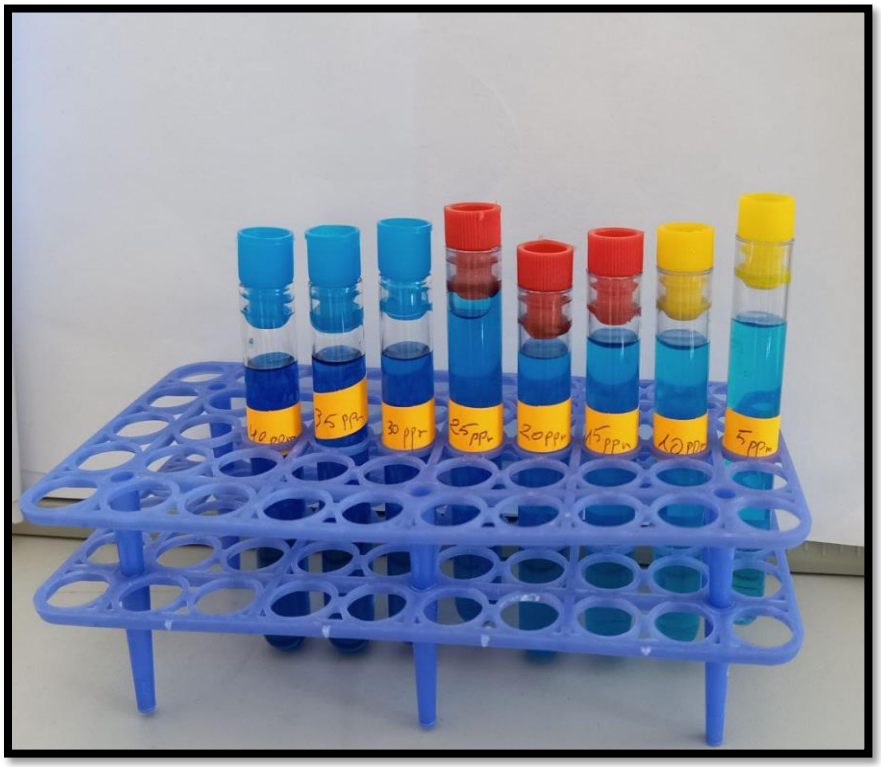


Figure (III.9): prepared standard solutions.

III.2.3. Response Surface Modelling (RSM)

To determine the optimal conditions for maximizing degradation, we subjected the results of this plan to statistical analysis.[1] In this study, we chose a Behnken-Box design BBD using the Design-Expert v13 software.[2]

The influential factors (mass, acidity level, contact time) were included in the Design-Expert v13 software, which provided 17 experiments with specific ranges and conditions. We conducted the experiments and calculated the removal efficiency of methylene bleu dye (MB). We obtained the best experiment with the highest removal efficiency.[3] [4] [5]

III.3. Work Plan

The aim of this work is to compare the efficiency of some metal oxides (titanium dioxide, manganese (II) dioxide) in decomposing methylene blue in aqueous medium at room temperature.

III.3.1. Step one

The absorption spectrum of methylene blue in an aqueous solution was obtained. Then a calibration curve was constructed by measuring the absorbance of each solution of the previously prepared standard solutions. The steps of this stage are illustrated in the following **figure (III.10).**

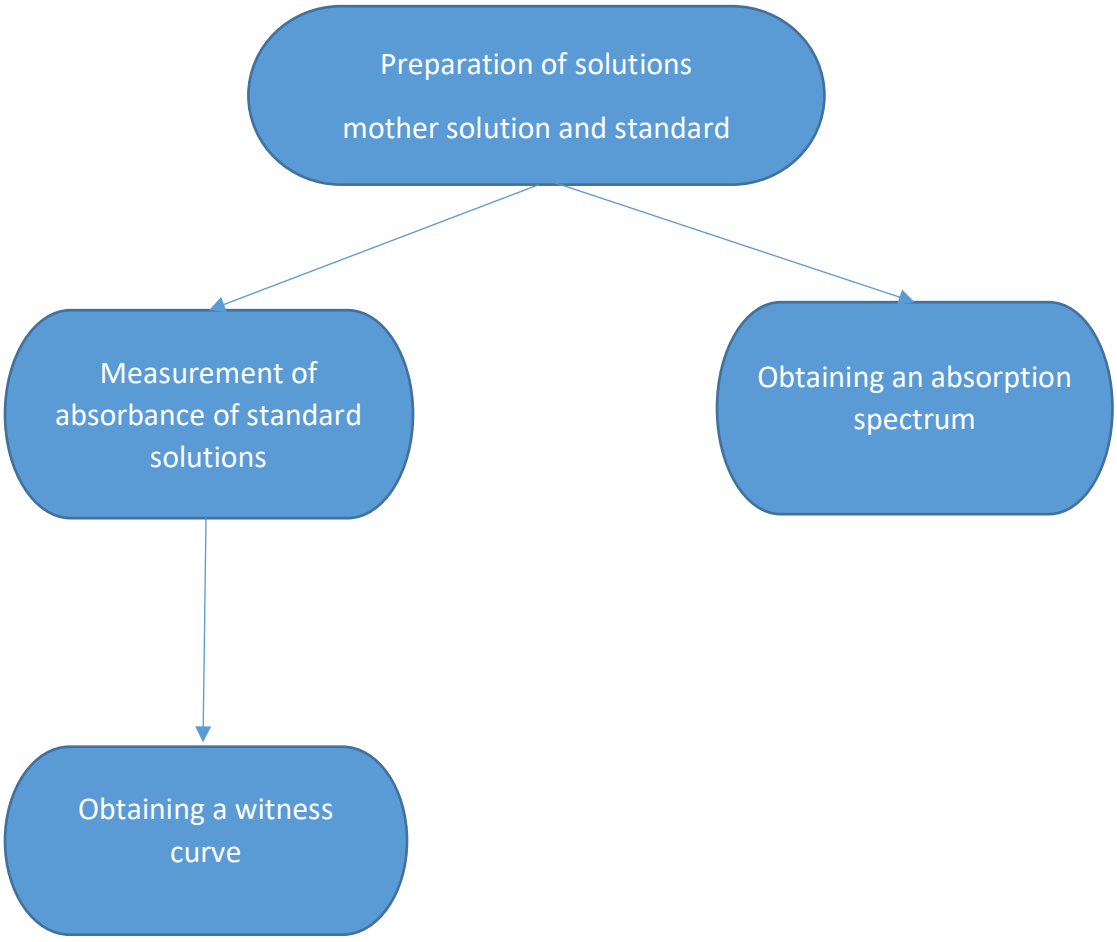


Figure (III.10): Diagram illustrating the steps for preparing the mother solution and Standard solutions of methylene blue

III.3.2. Step two

We prepared a non-homogeneous solution of metal oxide and a polluted aqueous solution. In each experiment, we varied the amount of catalyst**(TiO_2) (100mg,150mg,200mg)**. we prepared the same procedure for different solution for same catalyst amounts.

After that, we subjected the solution to a stirring process for one hour to reach the equilibrium state.

After this process, we performed centrifugation to separate the liquid form the solid metal oxide. Then, we measured the absorbance of the solution. The obtained absorbance is considered the initial absorbance $\mathbf{A_0}$ (before irradiation). We placed the solution in the irradiation device with continuous stirring until the solution becomes homogeneous and is exposed to the maximum possible light intensity.

At each interval, we took a sample to track the kinetics of the degradation. Then, we transferred the samples to a centrifuge to separate the liquid phase from the solid phase. Next, we took the liquid for analysis using a Visible/UV spectrophotometer to measure its absorbance.

The steps of the second step are illustrated in the **figure (III.11)**

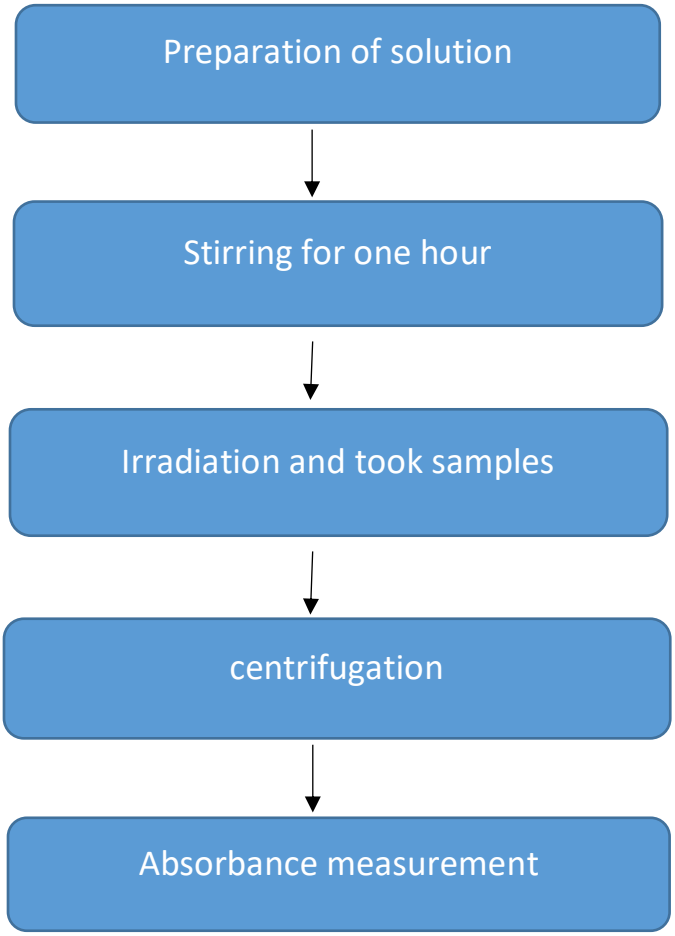


Figure (III.11): Diagram illustrating the steps involved in preparing and Analysing a solution.

III.3.3. Step three

we performed the same stages as in step 2, but we changed the pH of the solution in each case by adding drops of HCL solution (0,01M) to make the solution acidic, and drops of NaOH solution (0,01M) to make the solution basic. Then we placed each solution in the irradiation device and completed the same steps as before. The stages for this step are shown in **figure (III. 12).**

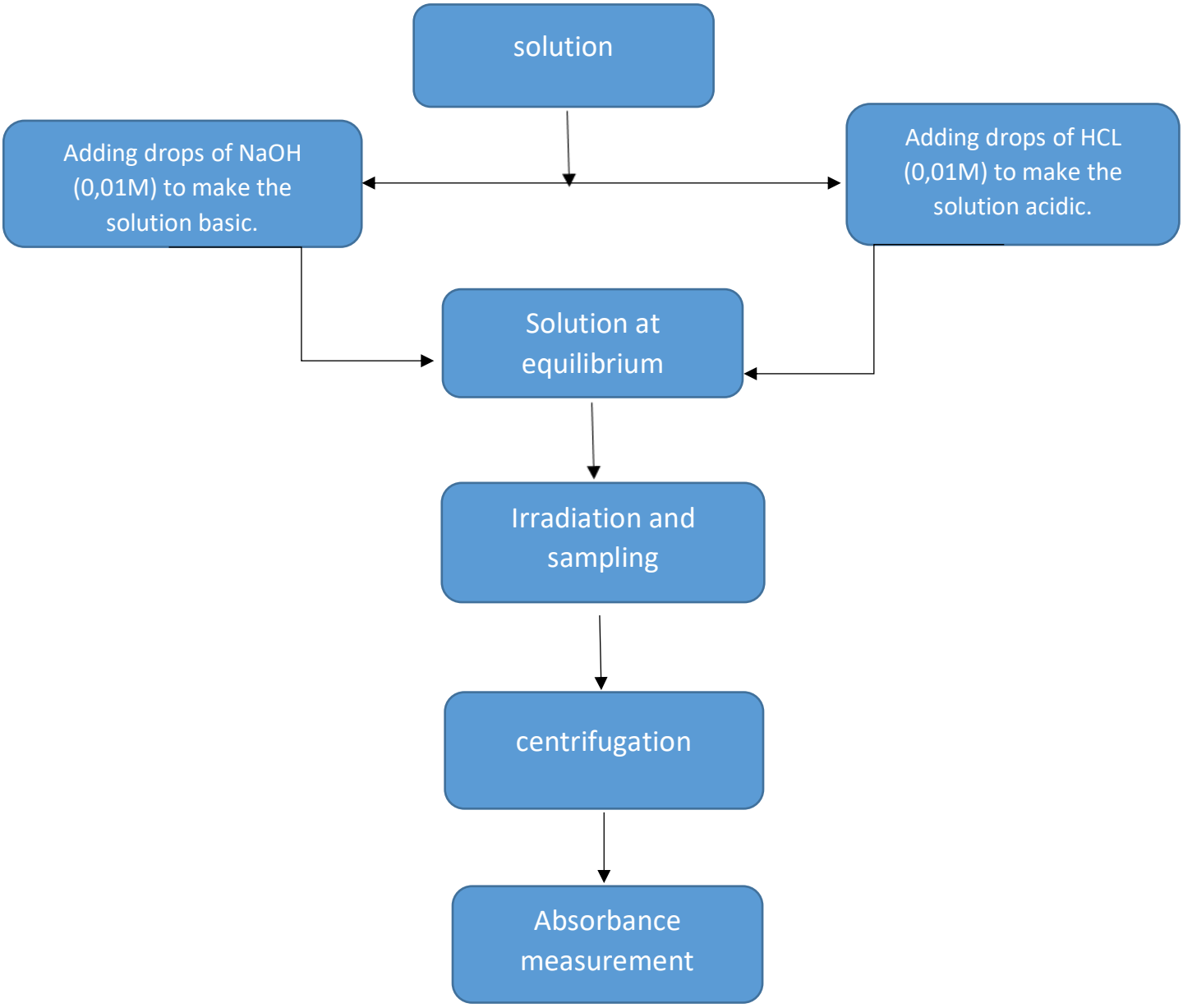


Figure (III.12): steps to study the effect of pH on the kinetics of degradation.

III.3.4. Step four

- We prepared a solution with varying concentrations from 8ppm to 32ppm and with a fixed pH of 7 and a catalyst (TiO_2) amount of 200mg at equal irradiation times (from 1 to 5 hours).

- We prepared a solution with varying concentrations from 8ppm to 32ppm and with a fixed pH of 7 and a catalyst (MnO_2) amount of 150mg at equal irradiation times (from 1 to 5 hours).

The same steps were repeated with manganese (IV) oxide (MnO_2).

References

References

[1] G. E. Box and D. W. J. T. Behnken, "Some new three level designs for the study of quantitative variables," vol. 2, no. 4, pp. 455-475, 1960.

[2] F. BENDAHMA, H. BENMEKKI, and B. ABSAR, "MEMOIRE DE FIN D'ETUDES DE MASTER ACADEMIQUE".

[3] N. T. T. Van *et al.*, "Cellulose from the banana stem: optimization of extraction by response surface methodology (RSM) and charaterization," vol. 8, no. 12, 2022.

[4] E. Oliva, "Nano-réacteurs à base de cyclodextrines amphiphiles pour la catalyse et la vectorisation ",Université de Picardie Jules Verne, 2019.

[5] A. Reghioua, D. Barkat, A. H. Jawad, A. S. Abdulhameed, A. A. Al-Kahtani, and Z. A. J. J. o. E. C. E. ALOthman, "Parametric optimization by Box–Behnken design for synthesis of magnetic chitosan-benzil/ZnO/Fe3O 4nanocomposite and textile dye removal," vol. 9, no. 3, p. 105166, 2021.

Chapter IV:
Results and Discussion

IV.1. Introduction

After preparing the mother solution and standard solutions for methylene blue, we analyzed them using UV-Vis spectrophotometry. All measurements were taken at room temperature and the following results were obtained:

IV.2. Spectral Analysis of MB

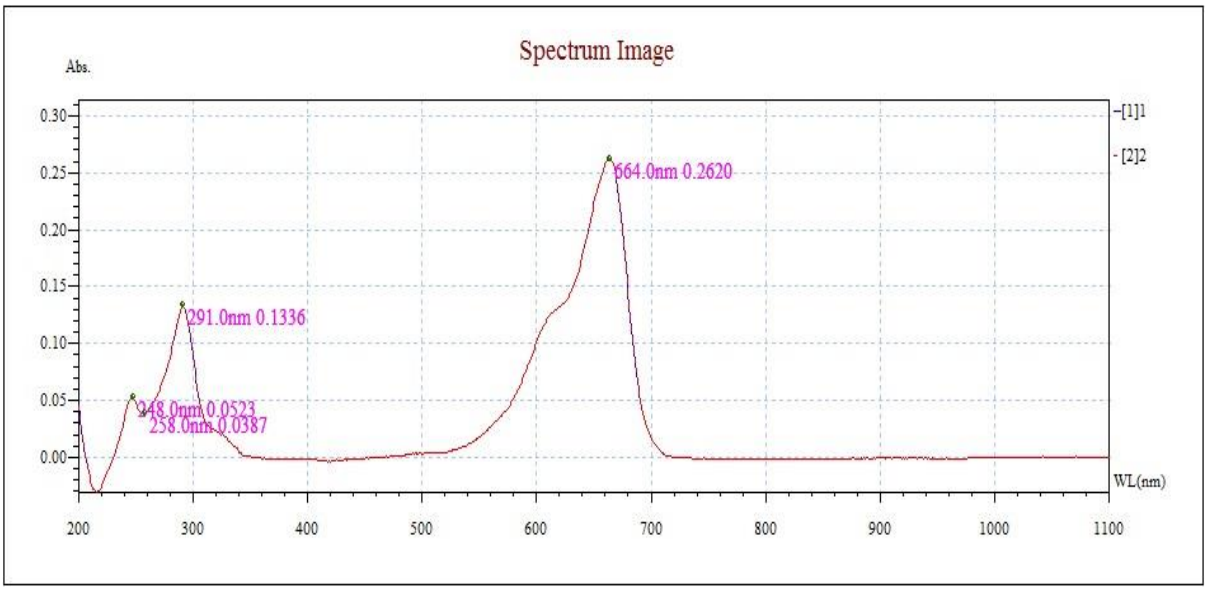
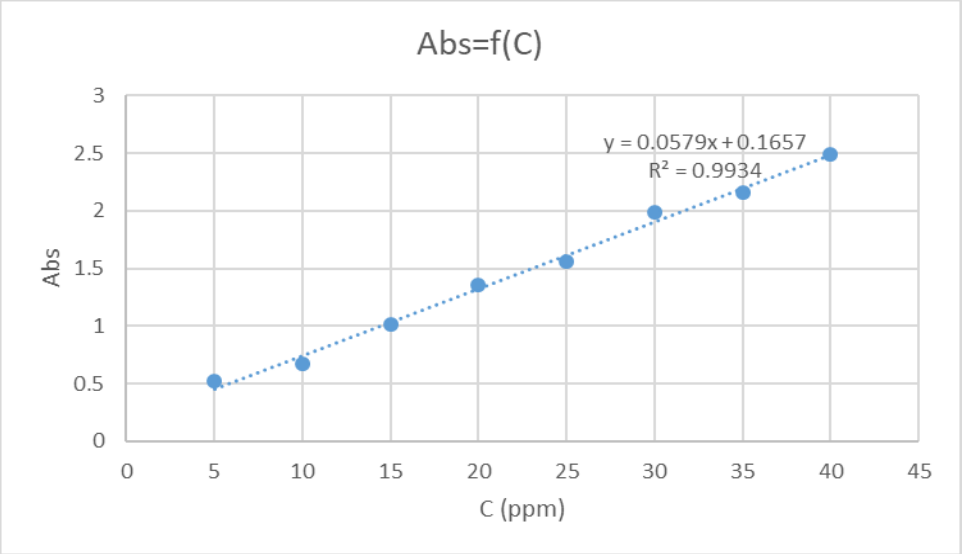


Figure (IV.1): determine λ_{max} of methylene blue

As observed in the absorption spectrum of methylene blue (Figure 1), the maximum absorption peak corresponds to a wavelength of 664 nm. This peak is attributed to the n-π transition, which is responsible for the characteristic color of this compound. A less intense peak is also observed in the ultraviolet region at 291 nm, arising from the π-π* transition.

IV.3.Witness Curve



Figure(IV. 2): Absorption-Concentration Curve of Methylene Blue Dye

IV.4. Response Surface Methodology (RSM) Modeling

Ⅳ.4.1. Determine the most effective method for removing methylene blue dye

A total of 34 experiments were conducted using the BBD model for both TiO_2 and MnO_2, with 17 experiments for each. After calculating the MB dye removal efficiency, it was found that the highest MB dye removal efficiency for TiO_2 was R= 49.64% and was achieved under the following experimental conditions: (B)pH=7 and (A) dose of TiO_2 200mg in 1 hour(C).

Table (IV. 01): Response Surface Methodology (RSM) results of TiO_2

Numéro	Dose(mg)	pH	Time(h)	R%
1	100	7	2	33.83
2	150	7	1.5	31.5
3	100	10	1.5	3.58
4	200	4	1.5	34.19
5	150	4	2	4.26
6	150	7	1.5	29.05
7	100	7	1	0.77
8	200	7	1	49.64
9	150	10	2	27.09
10	200	7	2	41.55
11	150	10	1	17.8
12	150	7	1.5	31.2
13	150	7	1.5	30.55
14	150	7	1.5	31.1
15	200	10	1.5	0.82
16	150	4	1	3.19
17	100	4	1.5	27.86

And the highest MB dye removal efficiency for MnO_2 was R= 46.3% and was achieved under the following experimental conditions:(B) pH=7 and (A) dose of MnO_2 150mg in 1 hour and helf (C).

Table (IV.02): Response Surface Methodology (RSM) results of MnO_2

Numéro	Dose(A)	pH(B)	Time(C)	R%
1	100	7	1	4.3
2	*150*	*4*	*1*	*33.51*
3	150	7	1.5	33.8
4	150	10	1	5.85
5	100	7	2	33.76
6	200	7	1	35
7	150	7	1.5	46.3
8	200	10	1.5	44
9	150	7	1.5	37.8
10	*100*	*10*	*1.5*	*7.23*
11	150	4	2	35
12	150	7	1.5	34.21
13	150	7	1.5	32.29
14	*200*	*7*	*2*	*40*
15	100	4	1.5	28.77
16	200	4	1.5	40.9
17	150	10	2	24.14

IV.4.2.BBD Model Analysis

A. The experimental data obtained from the BBD model was validated using Analysis of Variance (ANOVA).as shown in Table 3. ANOVA test revealed

the following values of TiO_2 : F = 13.66 and p < 0.0001. This indicates that the relationship between the input variables and the response variable (MB removal efficiency) is statistically significant.[1]

Table (IV.03): Analysis of variance (ANOVA) to remove MB dye of TiO_2

source	Sum of squares	df	Mean square	F-value	P-value	
Model	2254.28	9	250.48	1.16	0.432	not Significant
A-Dose	452.40	1	452.40	2.09	0.1911	
B-pH	51.06	1	51.06	0.2363	0.6417	
C-time	156.03	1	156.03	0.7223	0.4235	
AB	20.66	1	20.66	0.0956	0.7661	
AC	423.33	1	423.33	1.96	0.2043	
BC	16.89	1	16.89	0.0782	0.7878	
A^2	19.42	1	19.42	0.0899	0.7730	
B^2	1107.06	1	1107.06	5.12	0.0580	
C^2	8.02	1	8.02	0.0371	0.8527	
Residual	1512.13	7	216.02			
Lack of Fit	1508.34	3	502.78	530.22	< 0.0001	Significant
Pure Error	3.79	4	0.9482			
Cor Total	3766.41	16				
R^2	0.5985					
Adjusted R^2	0.0823					
Predicted R^2	-5.4091					
Adeq Precision	3.6151					

there is a discrepancy between the observed experimental values and the values predicted by the BBD model. This suggests that the model may not adequately capture the relationship between the input variables and the response variable (MB removal efficiency). he low coefficient of determination (R^2 = 0.0823) further reinforces this concern. R^2 measures the proportion of the variance in the response variable that is explained by the model. A low R^2 value suggests that the model is not explaining a significant portion of the variation in MB removal efficiency. Despite these inconsistencies, the analysis identified several factors that are considered significant contributors to MB removal efficiency: AB, C, B, A, C^2, B^2, A^2, AC. These factors can be incorporated into a predictive model for MB removal efficiency, as shown in the following equation:

$$R1 = + 30.68 + 7.52\,A - 2.53\,B + 4.42\,C - 2.27\,AB - 10.29\,AC + 2.05\,BC + 2.15\,A^2 - 16.22\,B^2 - 1.38\,C^2 \quad \text{.....(IV.1)}$$

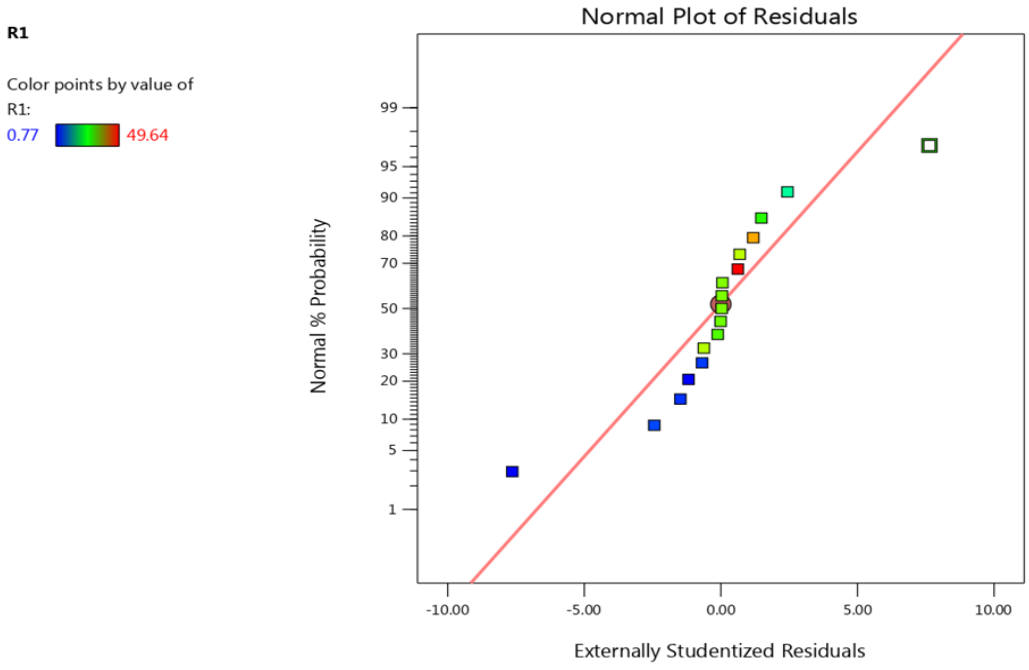


Figure (IV.3): Natural Probability in Terms of Examined External Residuals

the points in Figure (IV.3) are approximately evenly distributed along the first bisector. This observation implies that the proposed model is appropriate and reasonable .[2]

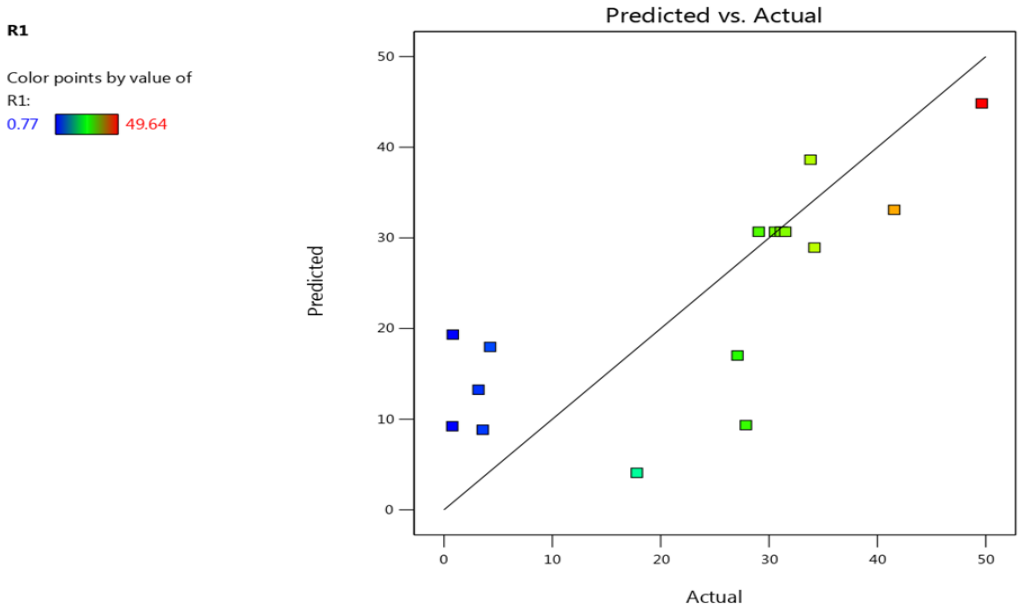


Figure (IV. 4): Relationship between Actual and Predicted MB Removal Efficiency

the observed and predicted data points in Figure (IV.4) are generally close to each other. This observation implies that the experimental results of the study are reliable and consistent with the theoretical predictions.

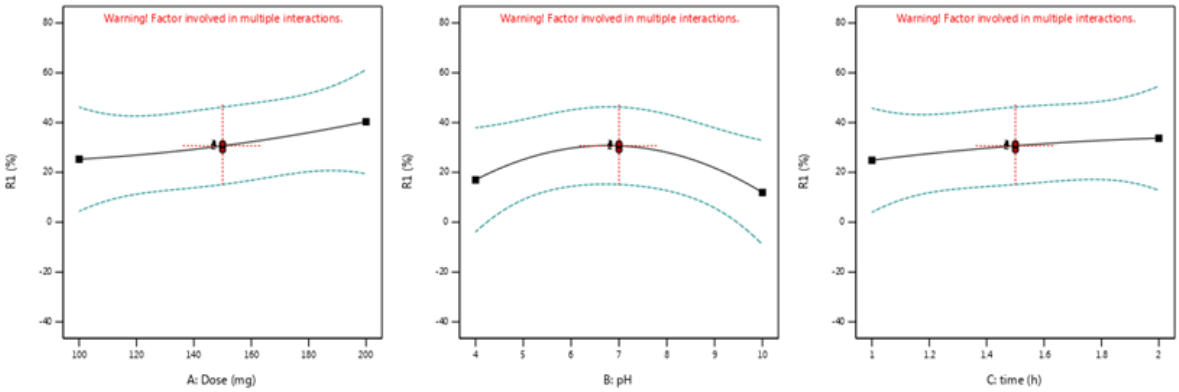


figure (IV.5): Investigation of the Influence of pH, Dose, and Time on MB Dye Removal Efficiency using BBD

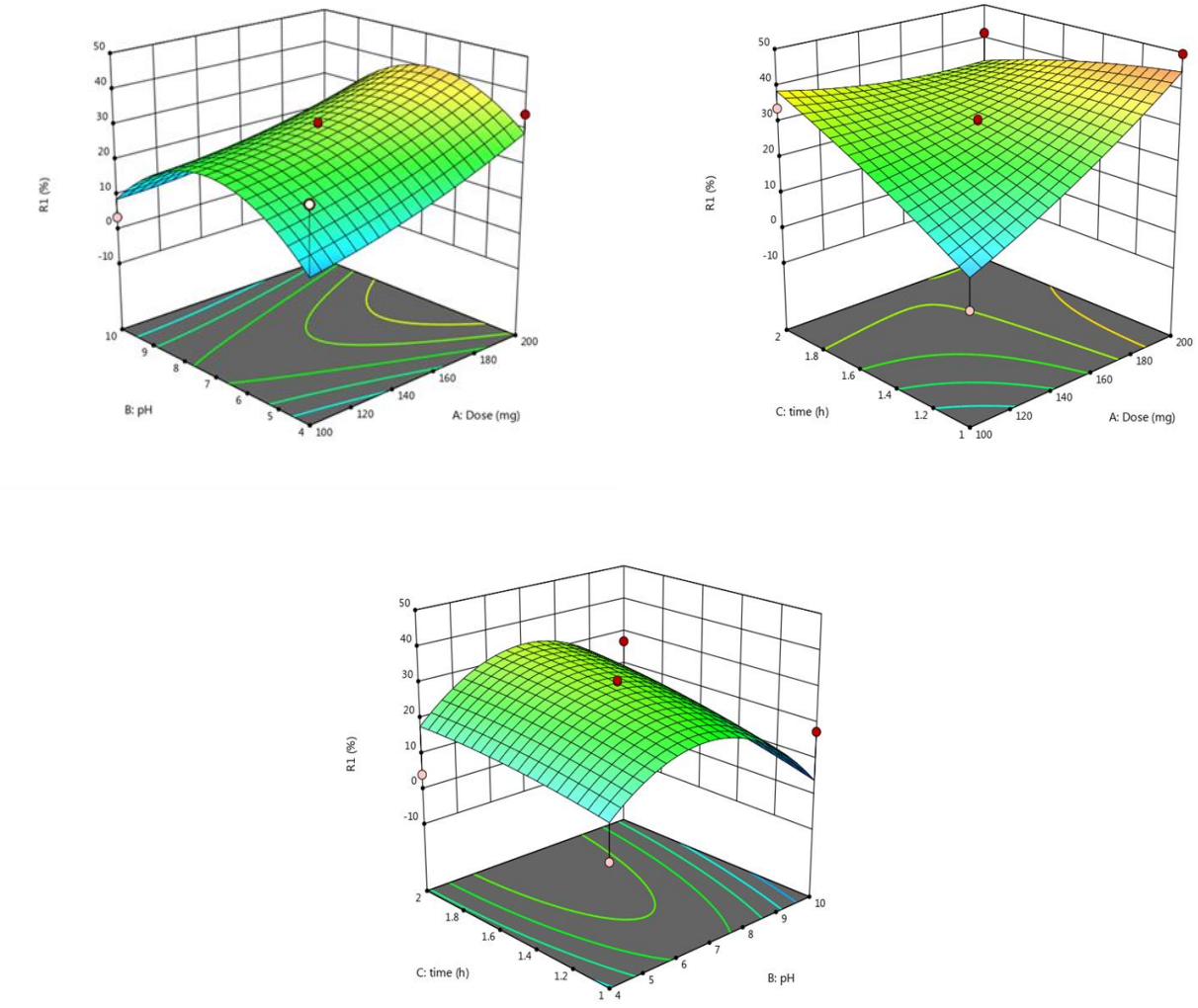


Figure (IV.6): Investigation of the Influence of Two Factors (pH , Time and Dose) on MB Dye Removal Efficiency using BBD

The variables Dose and Time have a direct and positive influence on the removal efficiency of MB dye using BBD. This observation is based on the data presented in Figures (IV.5) and (IV.6), which show an increasing trend in removal efficiency with increasing Dose and Time.

- **Dose (A):** Enhanced Photocatalytic Efficiency and Removal Efficiency with Increased Oxidant Dosage.
- **Time (C):** Extended Contact Time Facilitates Degradation of a Larger Proportion of Dye.

The indirect and inverse relationship between pH and removal efficiency. It suggests that increasing pH leads to a decrease in removal efficiency.

- **pH (B):** Enhanced Degradation Efficiency at Neutral pH . that a neutral pH environment is more favorable for the adsorption and subsequent degradation of dye molecules.

These findings align with the parameters of the Mb removal equation, where the coefficients for Dose and Time are positive, while those for pH are negative. This is evident in the equation (IV.1).

B. ANOVA test revealed the following values of MnO_2: $F = 8.49$ and $p < 0.0001$. In this model, a p-value lower than 0.05 is considered statistically significant. The observed and predicted values were found to be in close agreement, as evidenced by the high coefficient of determination ($R^2 = 0.8081$) (Table (IV.4)). This indicates that the model provides a good fit for the experimental data.

Table (IV.04): Analysis of variance (ANOVA) to remove MB dye of MnO_2

source	Sum of squares	df	Mean square	F-value	P-value	
Model	2427.9	9	269.78	8.49	0.0050	significant
A-Dose	921.06	1	921.06	28.98	0.0010	
B-pH	405.56	1	405.56	12.76	0.0091	
C-time	367.75	1	367.75	11.57	0.0114	
AB	151.78	1	151.78	4.78	0.0651	
AC	149.57	1	149.57	4.71	0.0667	
BC	70.56	1	70.56	2.22	0.1798	
A^2	9.57	1	9.57	0.3011	0.6003	
B^2	111.57	1	111.57	3.51	0.1031	
C^2	212.70	1	212.70	6.69	0.0361	
Residual	222.48	7	31.78			
Lack of Fit	95.22	3	31.74	0.9976	0.4798	not significant
Pure Error	127.27	4	31.82			
Cor Total	2650.48	16				
R^2	0.9161					
Adjusted R^2	0.8081					
Predicted R^2	0.3502					
Adeq Precision	8.6207					

Furthermore, the analysis revealed that AB, C, B, A, C^2, B^2, A^2, AC are significant factors influencing MB dye removal efficiency. Consequently, the MB dye removal efficiency can be expressed using a model equation that incorporates both significant and insignificant factors, as shown in the following equation:

$R1 = +36.88 + 10.73\ A - 7.12\ B + 6.78\ C + 6.16\ AB - 6.12\ AC + 4.2\ BC - 1.51\ A^2$

$-5.15\ B^2 - 7.11\ C^2$…..(IV.2)

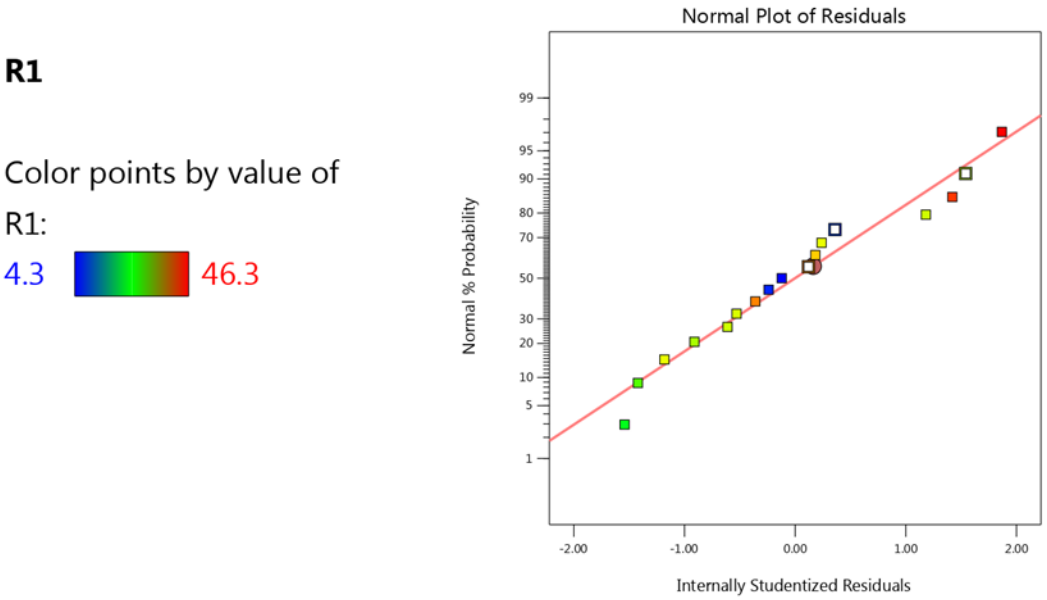


Figure (IV.7): Natural Probability in Terms of Examined External Residuals

the points in Figure (IV.7) are approximately evenly distributed along the first bisector. This observation implies that the proposed model is appropriate and reasonable [2]

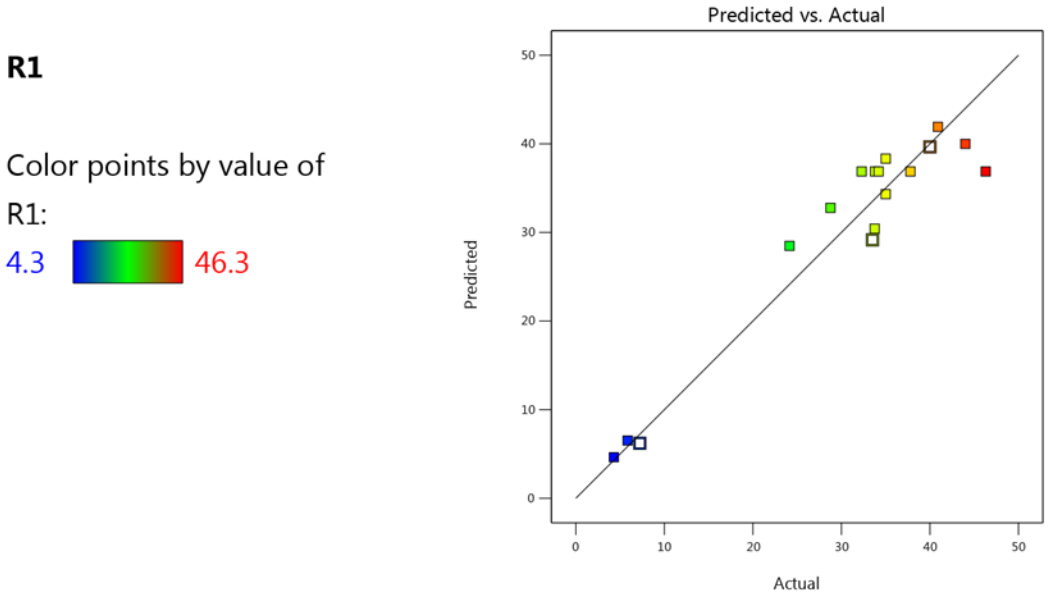


Figure (IV.8): Relationship between Actual and Predicted MB Removal Efficiency

the observed and predicted data points in Figure (IV.8) are generally close to each other. This observation implies that the experimental results of the study are reliable and consistent with the theoretical predictions

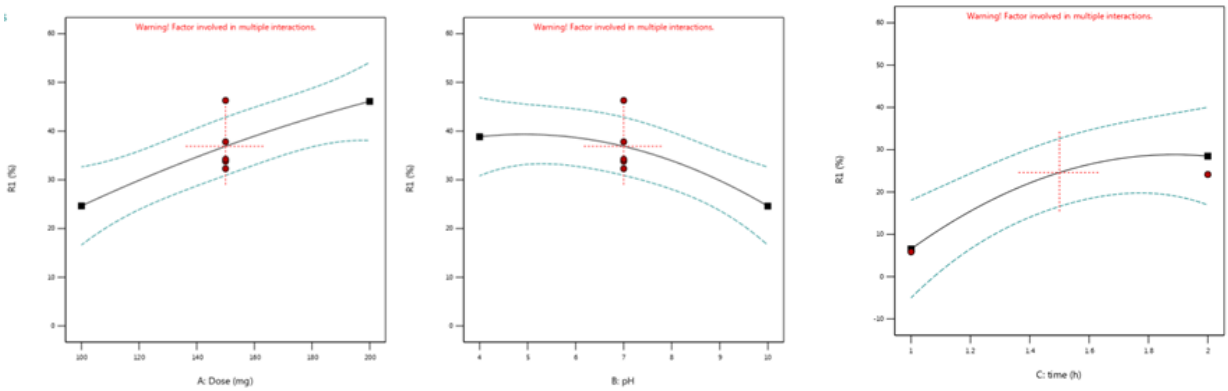


figure (IV.9) : Investigation of the Influence of pH, Dose, and Time on MB Dye Removal Efficiency using BBD

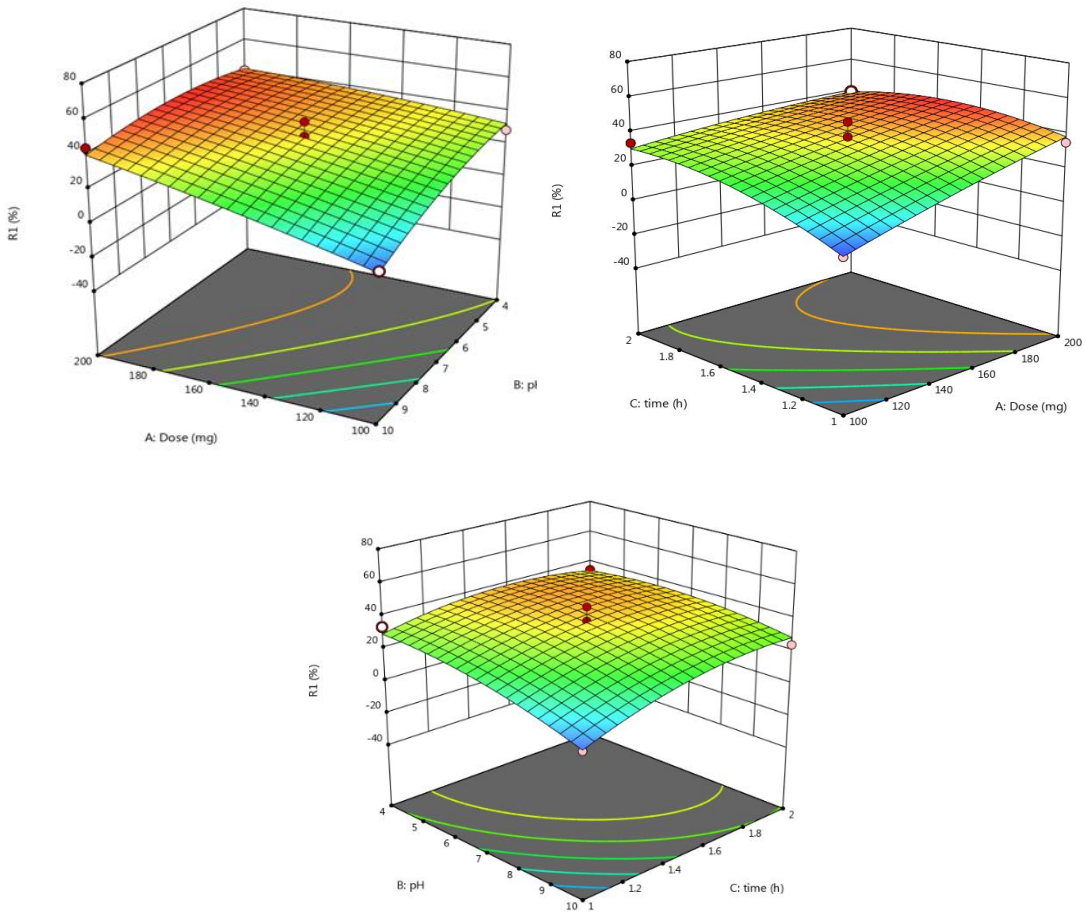


Figure (IV.10): Investigation of the Influence of Two Factors (pH , Time and Dose) on MB Dye Removal Efficiency using BBD

The variables Dose and Time have a direct and positive influence on the removal efficiency of MB dye using BBD the same as the TiO_2 . The figure (IV.9) and (IV.10) which show an increasing trend in removal efficiency with increasing Dose and Time.

- **Dose (A):** Enhanced Photocatalytic Efficiency and Removal Efficiency with Increased Oxidant Dosage.

- **Time (C):** Extended Contact Time Facilitates Degradation of a Larger Proportion of Dye.

The indirect and inverse relationship between pH and removal efficiency. It suggests that increasing pH leads to a decrease in removal efficiency.

- **pH (B):** Enhance decomposition efficiency at neutral and acidic pH . And neutral pH environment is more favorable for the absorption and subsequent degradation of dye molecules.

These findings align with the parameters of the Mb removal equation, where the coefficients for Dose and Time are positive, while those for pH are negative. This is evident in the equation (IV.2).

IV.5. Investigation of Degradation-Influencing Factors

IV.5.1. Investigating Concentration Effect

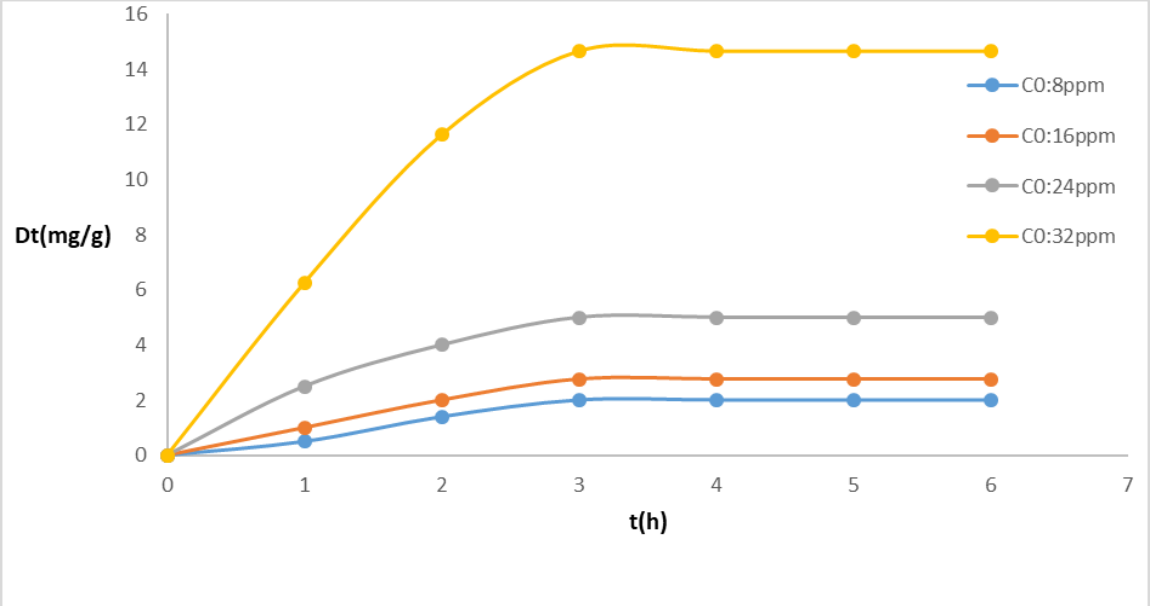


Figure (IV.11): Concentration-Time Curve of Degradation Quantity of TiO_2

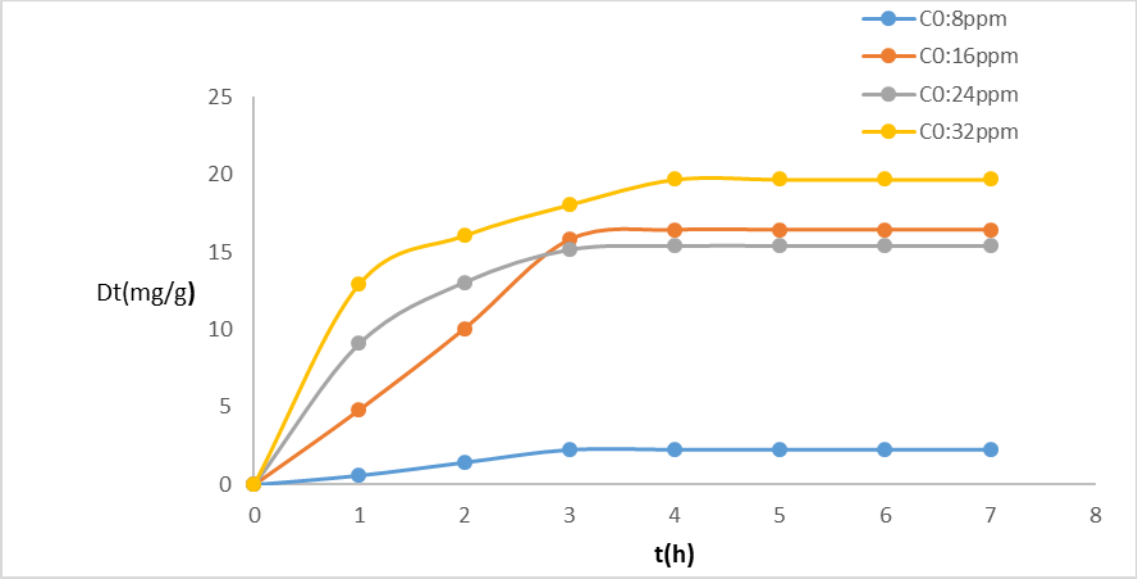


Figure (IV.12): Concentration-Time Curve of Degradation Quantity of MnO_2

The results depicted in the figure above demonstrate a positive correlation between the degradation of MB dye and reaction time. Initially, the degradation rate (De) exhibited a rapid increase, primarily attributed to the high activity of the photocatalyst . However, as the reaction progressed, the degradation rate gradually declined due to the saturation of active sites on the catalyst surface.[3]

a) The TiO_2 results

- Degraded quantity: 4.65 mg/g
- Dye concentration: 8 ppm
- Reaction time: 3 hours

b) The MnO_2 results

- Degraded quantity: 2.28 mg/g
- Dye concentration: 8 ppm
- Reaction time: 3 hours

These conditions were selected based on the observation that the amount of catalyst significantly exceeds the number of MB dye ions present in the solution. This excess of catalyst ensures that all dye molecules have ample opportunity to interact with and be degraded by the catalyst surface.

IV.5.2. Degradation kinetics

Table (IV.05): Kinetic Study of MB Dye Degradation Using TiO_2 results

C0	De(exp)	Pseudo first order			Pseudo second order		
		De(cal)	K1	R^2	De (cal)	K2	R^2
8	2.01	2.30	0.46	0.85	3.22	0.11	0.81
16	2.76	3.02	0.55	0.90	4.00	0.12	0.85
24	5.00	5.23	0.73	0.95	6.42	0.12	0.89
32	14.67	15.61	0.65	0.92	19.79	0.03	0.86

Table (IV.06): Kinetic Study of MB Dye Degradation Using MnO_2 results

C0	De(exp)	Pseudo first order			Pseudo second order		
		De(cal)	K1	R^2	De (cal)	K2	R^2
8	2.28	2.51	0.48	0.85	3.36	0.12	0.81
16	16.43	18.08	0.47	0.89	24.16	0.02	0.84
24	15.4	15.65	0.91	0.98	17.96	0.07	0.90
32	19.68	19.65	0.98	0.95	22.25	0.06	0.96

This observation suggests that the photocatalytic degradation of MB dye follows a pseudo-first-order kinetic model, The pseudo-first-order kinetic model ($D_{e.cal}$) exhibited a better fit to the experimental data ($D_{e.exp}$) compared to the pseudo-second-order model. This is supported by the higher R^2 value obtained for the pseudo-first-order model, indicating a stronger correlation between the model predictions and the experimental observations.[4]

Reference

Reference

[1] J. Qu, X. Meng, H. You, X. Ye, and Z. J. B. t. Du, "Utilization of rice husks functionalized with xanthates as cost-effective biosorbents for optimal Cd (II) removal from aqueous solution via response surface methodology," vol. 241, pp. 1036-1042, 2017.

[2] B. T. Iber *et al.*, "Optimization of chitosan coagulant from dry legs of giant freshwater prawn, Macrobrachium rosenbergii in aquaculture wastewater treatment using response surface methodology (RSM)," vol. 11, no. 3, p. 109761, 2023.

[3] S. M. Tichapondwa, J. Newman, O. J. P. Kubheka, and P. A. B. C. Chemistry of the Earth, "Effect of TiO2 phase on the photocatalytic degradation of methylene blue dye," vol. 118, p. 102900, 2020.

[4] A. Benhouria, H. Zaghouane-Boudiaf, R. Bourzami, F. Djerboua, B. Hameed, and M. J. I. J. o. B. M. Boutahala, "Cross-linked chitosan-epichlorohydrin/bentonite composite for reactive orange 16 dye removal: Experimental study and molecular dynamic simulation," vol. 242, p. 124786, 2023.

GENERAL CONCLUSION

GENERAL CONCLUSION

In this research, a comparative study was conducted to investigate the photocatalytic efficiency of two metal oxides, titanium dioxide (TiO_2) and manganese dioxide (MnO_2), in the degradation of methylene blue, a common organic pollutant. These oxides are classified as semiconductors with bandgaps falling within the visible and ultraviolet regions, enabling their use as photocatalysts.

The study focused on examining the influence of medium pH on the pollutant degradation rate in the presence of these photocatalysts (oxides) individually under neutral (pH=7), acidic (pH=4), and alkaline (pH=10) conditions at varying irradiation times and oxide concentrations.

The obtained results confirmed the following:

- TiO_2 exhibited superior photocatalytic performance compared to MnO_2 under all pH conditions. Under neutral conditions (pH=7), TiO_2 successfully degraded 49.64% of the pollutant within an hour of irradiation, while MnO_2 achieved a 46.3% degradation rate after one hour and 30 minutes. This difference in performance is attributed to the wider bandgap of MnO_2, which limits its light absorption and photoexcitation capabilities.
- The degradation efficiency of both TiO_2 and MnO_2 was found to increase with increasing oxide concentration up to an optimal point. This suggests that a higher concentration of active sites leads to enhanced photocatalytic activity. However, beyond the optimal concentration, the degradation efficiency tends to decrease due to light scattering and competition for light absorption among oxide particles.
- The degradation kinetics of methylene blue in the presence of TiO_2 (degradation rate De = 10.74 mg/g) and MnO_2 (degradation rate De = 18.23 mg/g) followed a pseudo-first-order rate model under all pH conditions. This indicates that the rate of degradation is proportional to the concentration of the remaining pollutant.

The findings of this study highlight the potential of TiO_2 as an effective photocatalyst for the degradation of organic pollutants, particularly under neutral pH conditions. The influence of pH and oxide concentration on degradation efficiency provides valuable insights for optimizing photocatalytic treatment processes.

We hope to continue this research in the future by investigating the impact of temperature on the degradation rate, identifying the chemical composition of the photodegradation products, assessing their toxicity, and achieving complete mineralization of the pollutant. By doing so, we aim to make a modest contribution to alleviating the burden of toxic substances and compounds that have long plagued scientists and researchers.

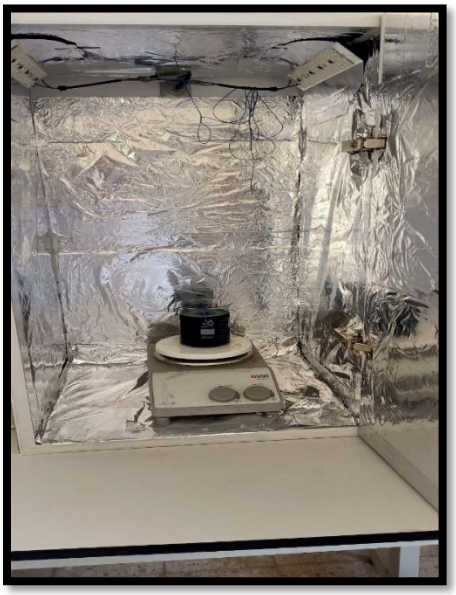
APPENDIX

Pictures:

Electronic sensitive scale machine

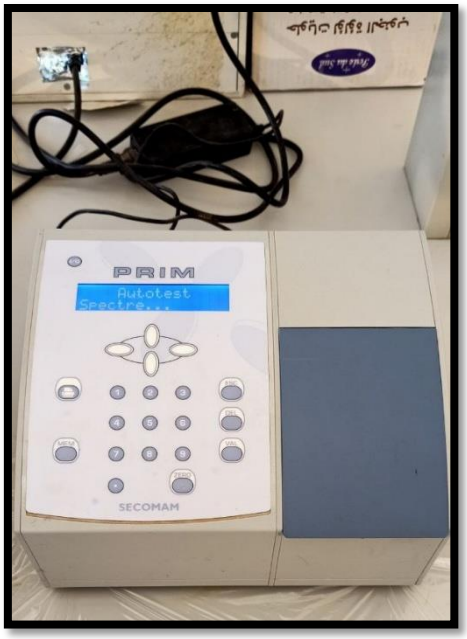
Magnetic resonance imaging

Instrument pH meter.

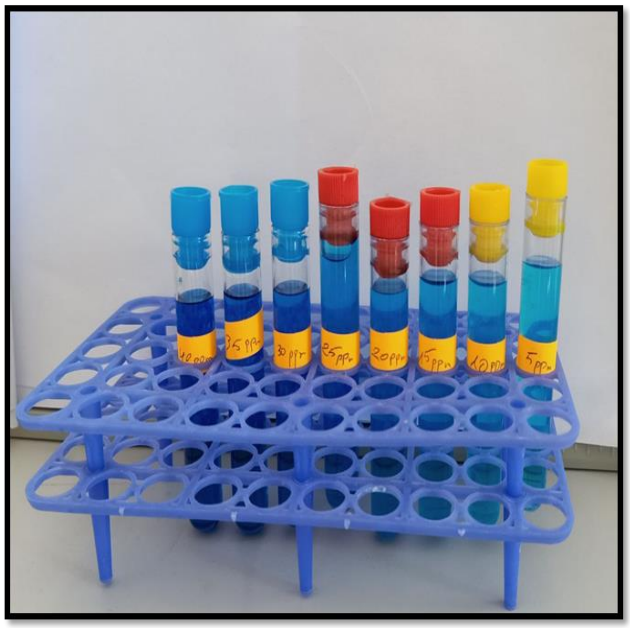


Internal radiation therapy

Centrifuge



Ultraviolet-visible spectrometer



prepared standard solutions.

Solution of BM

Tables :

Table 1 : witness curve result

C(ppm)	5	10	15	20	25	30	35	40
Abs	0.518	0.673	1.012	1.631	1.555	1.991	2.158	2.486

Table 2: Response Surface Methodology (RSM) results of TiO_2

Numéro	Dose(mg)	pH	Time(h)	R%
1	100	7	2	33.83
2	150	7	1.5	31.5
3	100	10	1.5	3.58
4	200	4	1.5	34.19
5	150	4	2	4.26
6	150	7	1.5	29.05
7	100	7	1	0.77
8	200	7	1	49.64
9	150	10	2	27.09
10	200	7	2	41.55
11	150	10	1	17.8
12	150	7	1.5	31.2
13	150	7	1.5	30.55
14	150	7	1.5	31.1
15	200	10	1.5	0.82

16	**150**	**4**	**1**	**3.19**
17	**100**	**4**	**1.5**	**27.86**

Table 3: Response Surface Methodology (RSM) results of MnO_2

Numéro	Dose(A)	pH(B)	Time(C)	R%
1	**100**	**7**	**1**	**4.3**
2	***150***	***4***	***1***	***33.51***
3	**150**	**7**	**1.5**	**33.8**
4	**150**	**10**	**1**	**5.85**
5	**100**	**7**	**2**	**33.76**
6	**200**	**7**	**1**	**35**
7	**150**	**7**	**1.5**	**46.3**
8	**200**	**10**	**1.5**	**44**
9	**150**	**7**	**1.5**	**37.8**
10	***100***	***10***	***1.5***	***7.23***
11	**150**	**4**	**2**	**35**
12	**150**	**7**	**1.5**	**34.21**
13	**150**	**7**	**1.5**	**32.29**
14	***200***	***7***	***2***	***40***
15	**100**	**4**	**1.5**	**28.77**
16	**200**	**4**	**1.5**	**40.9**
17	**150**	**10**	**2**	**24.14**

Table 4: Analysis of variance (ANOVA) to remove MB dye of TiO_2

source	Sum of squares	df	Mean square	F-value	P-value	
Model	2254.28	9	250.48	1.16	0.432	not Significant
A-Dose	452.40	1	452.40	2.09	0.1911	
B-pH	51.06	1	51.06	0.2363	0.6417	
C-time	156.03	1	156.03	0.7223	0.4235	
AB	20.66	1	20.66	0.0956	0.7661	
AC	423.33	1	423.33	1.96	0.2043	
BC	16.89	1	16.89	0.0782	0.7878	
A^2	19.42	1	19.42	0.0899	0.7730	
B^2	1107.06	1	1107.06	5.12	0.0580	
C^2	8.02	1	8.02	0.0371	0.8527	
Residual	1512.13	7	216.02			
Lack of Fit	1508.34	3	502.78	530.22	< 0.0001	Significant
Pure Error	3.79	4	0.9482			
Cor Total	3766.41	16				
R^2	0.5985					
Adjusted R^2	0.0823					
Predicted R^2	-5.4091					
Adeq Precision	3.6151					

Table 5: Analysis of variance (ANOVA) to remove MB dye of MnO_2

source	Sum of squares	df	Mean square	F-value	P-value	
Model	2427.9	9	269.78	8.49	0.0050	significant
A-Dose	921.06	1	921.06	28.98	0.0010	
B-pH	405.56	1	405.56	12.76	0.0091	
C-time	367.75	1	367.75	11.57	0.0114	
AB	151.78	1	151.78	4.78	0.0651	
AC	149.57	1	149.57	4.71	0.0667	
BC	70.56	1	70.56	2.22	0.1798	
A^2	9.57	1	9.57	0.3011	0.6003	
B^2	111.57	1	111.57	3.51	0.1031	
C^2	212.70	1	212.70	6.69	0.0361	
Residual	222.48	7	31.78			
Lack of Fit	95.22	3	31.74	0.9976	0.4798	not significant
Pure Error	127.27	4	31.82			
Cor Total	2650.48	16				
R^2	0.9161					
Adjusted R^2	0.8081					
Predicted R^2	0.3502					
Adeq Precision	8.6207					

Table 6: Kinetic Study of MB Dye Degradation Using TiO_2 results

C0	De(exp)	Pseudo first order			Pseudo second order		
		De(cal)	K1	R^2	De (cal)	K2	R^2
8	2.01	2.30	0.46	0.85	3.22	0.11	0.81
16	2.76	3.02	0.55	0.90	4.00	0.12	0.85
24	5.00	5.23	0.73	0.95	6.42	0.12	0.89
32	14.67	15.61	0.65	0.92	19.79	0.03	0.86

Table 7: Kinetic Study of MB Dye Degradation Using MnO_2 results

C0	De(exp)	Pseudo first order			Pseudo second order		
		De(cal)	K1	R^2	De (cal)	K2	R^2
8	2.28	2.51	0.48	0.85	3.36	0.12	0.81
16	16.43	18.08	0.47	0.89	24.16	0.02	0.84
24	15.4	15.65	0.91	0.98	17.96	0.07	0.90
32	19.68	19.65	0.98	0.95	22.25	0.06	0.96