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Faculty of Sciences  
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**End of study dissertation**

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**ACADEMIC MASTERS**

**In organic chemistry**

**THEME**

**Extraction of organic dyes by adsorption method  
using  
NiO-MgO nanoparticles**

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**Soutenu le 12-07-2022**

**In front of the jury:**

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## Abstract :

In the present work, we are interested to the study of the adsorption of Malachite green, it is cationic dye. For this work we use catalyst NiO-MgO synthesised by two methods autocombustion and impregnation, calcinated at 700°C for 2h, characterizes by XRD and SEM analysis than applied on the elimination of Malachite green by adsorption process. The experimental results showed that the NiO-MgO prepared with autocombustion is more efficient in adsorption than NiO-MgO impregnation due to the IP due to the smallest crystallite size 8 nm compared to 28nm in case of NiO-MgO AT. The study of the influence of the pH dye, the initial concentration of pollutant and the adsorbent mass showed us that the optimal adsorption of malachite green is on this condition ( $C_0= 30$  ppm,  $pH=10$ ,  $T=25^\circ C$ ,  $m=0.04$  g) after 55 min of reaction.

## Résumé :

Dans le présent travail, nous intéressons à l'étude de l'adsorption du vert de malachite, sur le matériaux qui est un colorant cationique. Pour cela nous choisisant le catalyseur NiO-MgO synthétisé par deux méthodes autocombustion et imprégnation, calciné à 700°C pendant 2h, caractérisé par DRX et analyse MEB puis appliqué dans le procédé d'élimination du vert de malachite par d'adsorption. Les résultats expérimentaux ont montré que le NiO-MgO préparé avec autocombustion est plus efficace en adsorption que l'imprégnation NiO-MgO en raison de la plus petite taille de cristallite 8 nm par rapport à 28 nm en cas de NiO-MgO préparé par imprégnation. L'étude de l'influence du pH du colorant, de la concentration initiale en polluant et de la masse de l'adsorbant nous a montré que l'adsorption optimale du vert de malachite s'effectue dans les conditions suivants ( $C_0= 30$  ppm,  $pH=10$ ,  $T=25^\circ C$ ,  $m= 0,04$  g) et cela après 55 min de réaction.

## ملخص

العمل الحالي، الذي نحن مهتمون بدراسة اخضر الملاكيت، هو صبغه كا تو نية. لهذا استعملنا المحفز NiO-MgO المصطنع بطريقتين الاحتراق الذاتي والتشريب. المكلس عند 700 درجة مئوية لمده ساعتين. قمنا بتحليل المحفز بطريقتين XRD و SEM. أظهرت هذه التحاليل ان NiO-MgO (AT) هو اصغر حجم بلوري بمعدل 8 نانومتر مقارنة بـ  
ب

NiO-MgO (IP) الذي يبلغ 28 نانومتر. وبالتالي فاننا نستنتج ان NiO-MgO المصطنع بطريقة الاحتراق التلقائي هو أكثر كفاءة في الامتزاز ثم يليه التشريب. دراسته تأثير هذه الصبغة والتركيز الاولي الملوثات اظهرت لنا ان الامتزاز الامثل لاخضر الملاكيت موجود في هذه الشروط، ( $C_0=30$ ) جزء في مليون. درجة الحموضة =10،  $T=25$ ،  $m=0.04$  جرام بعد 55 دقيقة من التفاعل.

## **Thank You**

First and foremost, I thank God, Almighty, for giving me the strength and audacity to overcome all the difficulties.

At the end of this study, I am pleased to sincerely ask all those who, thanks to their invaluable help, have made it possible to carry out this work and in particular:

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I would like to express my deep gratitude to my driving force yahi nora for his beneficial advice and his support that he stopped giving me throughout this work.

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All the teachers in the chemistry department trained me and gave me their valuables.

## **Dedications**

I dedicate the fruit of this modest work:

To my dear families for their love, their patience and their encouragement which never ceased to please me during my years of study.

To my dear sister ♡chahinaz♡ for the moral support and encouragement in my moments of doubt and the trust she has given me.

To my cousin ♡Amine♡.

To my friends ♡ yousra, Amina ♡.

To all those who are dear to me.

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## **General Introduction**

Everything God created in this life is in purpose like colors have a psychological effect and physical effect. Humans have invested in the revolution of colors by the years and use it in different domains.

Industry is also responsible for more than half of total emissions of certain air pollutants and greenhouse gases, as well as other significant environmental impacts, including the release of pollutants to water and soil, the production of waste and energy consumption. Knowing that

Industry is an essential pillar of the European economy. According to Eurostat, in 2018 it accounted for 17.6% of gross domestic product (GDP) and directly employed 36 million people.

Chemical pollution is a kind of the type of water pollution due for example of rejected dye, this pollution generally comes from wastewater discharges containing cleaning products, hydrocarbons and heavy metals. It has been estimated that 15% of total dyes produced worldwide are discharged to water bodies which adversely affect aquatic ecosystem. Approximately 1-2% of dye stuffs are lost during production and about 10-15% of dyes are discharged as effluent during dye applications.

Green malachite is useful for many domains we distinguish a few : Chemistry and dyeing, Pharmacy, Biology, food sector. Malachite green in its uses it protects aquatic sources and especially fish to fight against the dangers of mycoses and fungi in eggs, fry and young fish in fish farming. It is used in combination with formalin and Methylene Blue to fight against : Oodinium (velvet disease), Saprolegniosis (cottony mold), Ichthyophthiriosis (white spot disease) or Gyrodactylosis (disease skin worms), also used as treatment for fish stress.

But the coin has two sides so that this dye has a dangerous effect on health. Living things have mitochondria that by green of malachite are destroyed. This takes place through an inhibition of respiratory enzymes. The VM molecule interacts with DNA to alter its functions and structure, VM is mutagenic and carcinogenic. This effects for animals but let's talk about human it would have effects on the immune system, the reproductive system, in addition to having teratogenic properties (creation of abnormal cells, and child malformation in pregnant women) and carcinogenic properties.

In our work we are interested in the elimination of green malachite dye which by adsorption in material NiO-MgO. In chapter 1 is the bibliographical study, chapter 2 synthesis of materials

NiO-MgO by two methods autocombustion (AT) and impregnation (IP), and the final chapter is chapter 3 is about results and discussion.

**CHAPTER I :BIBLIOGRAPHICAL  
STUDY**

## Introduction

Imagine with me a world without colors so that everything is seen as neutral. Since ancient times, man was created to enjoy colors which reflect beauty. A dye is a substance used to add color to an object to be colored in order to give it life. In chemistry, a group of atoms whose absorption of light causes a color to be called a chromophore. So that; a dye is a colored substance that is chemically related to the substrate on which it is applied. When the color of substrates is modified; the most varied natural and synthetic textiles paper, leather furs, plastic materials, rubbers like waxes cosmetics. Most dyes are organic compounds (i.e. contain carbon); while dyes may be inorganic compounds (i.e. do not contain carbon).

There are two main families of colorants: natural dyes (extracted from mineral or organic matter) and those resulting (from chemical synthesis reference)

The oldest known dyes in the world are those used in the Lascaux Caves in France. They date from the Palaeolithic (around 15,000 BC). It was natural dyes (mineral pigments). which of the earth. Around 1500 BC, the Egyptians used saffron, pastel and madder as dyes. Until 1850, all the dyes used in food were natural (chlorophyll for green, charcoal for black, etc.).

This is for natural dyes, but the first to discover artificial coloring is by the English chemist of origin William Perkin in 1856. The synthetic process was based on the oxidation of allyltoluidine (which is a petroleum derivative). This dye was named aniline purple (or mauveine). It was used in the coloring of textiles.

In this chapter we first recalled the large families' dyestuff chemicals which make up the large share of the dyestuff market industrial.

### I.1.Synthetic dyes:

Dyes are organic chemicals that absorb and reflect light contains two parts:

*Chromophores*: It has groups that give it color and another part *Auxochromes*: their function is to enhance, intensify and deepen color.

**I.1. a. General:**

Over the years, natural wealth has decreased. Therefore, natural dyes have become very expensive. Since the beginning of the 19th century, the dyes started to be adopted as an alternative of natural dyes. As a result, many families of dyes were created. They are similar to the structure of natural dyes. Surinanity led or encouraged the development of scientific research in the field of chemistry.

Mauveine, the first synthetic dye accidentally discovered by WILLIAM HARRY PERKIN in 1856. It was obtained from aniline (derived from coal) by the action of sulfuric acid and the presence of sodium bicarbonate, potassium made it possible to dye silk with purple color then, the so called azo dye was discovered in England in 1860, and it became an alternative to aniline based dyes on the grounds that light resistance is weak.

**I.1.2. Textile Dyes: definitions and structures:**

There are three transformations of white light either by reflection, transmission or scattering. The dye absorbs light radiation in the visible spectrum (380/750nm) by converting white light into a light color. It results from the selective adsorption of energy by certain groups of atoms called (CHROMOPHORES) and the molecular pigment is the chrom. The easier the chromophore group is to donate a larger electron, the more intense the color. Chromophore groups started by intensity decrease (Table 1). Other groups of atoms in the chromogen may condense or change color due to the chromophore: these are auxochrome groups.

Chromophores are aromatic groups (electrons), conjugated (bonds) comprising unbonded pairs (n-electrons) or complexes of transition metals.

The dyes differ from each other by combinations of molecular orbitals. The coloration corresponds to the potential transitions after adsorption of light radiation between these energy levels appropriate for each molecule.

The dye consists of two main groups: chromophores and auxochromes with aromatic conjugate structures represented by (benzene, anthracene, perylene, etc).

The textile coloring industry is a service industry that changes the appearance and the aesthetics of textile materials. So that, coloring in this industry is particularly important for Apparel fabrics and for many other and uses such as carpets, upholstery fabrics, automobile textiles, and military textiles. [1]

### **I.1.3. Nature Dyes:**

#### **I.1.3.a. Chromophore group:**

Moving electrons are originally adsorbers of light radiation in the direction of long wavelengths. There are a compo of unsaturated functional group but must bind to other chromophore is that part of the molecule to be colored. The chromophore is that part of the molecule where the adsorption continues and where the major change in geometry or electron density. [2.3]

A chromophore is that part of the molecule where the absorption proceeds and where the main change of the geometry or electron density, etc. [4]

#### **I.1.3.b. Auxochromic group:**

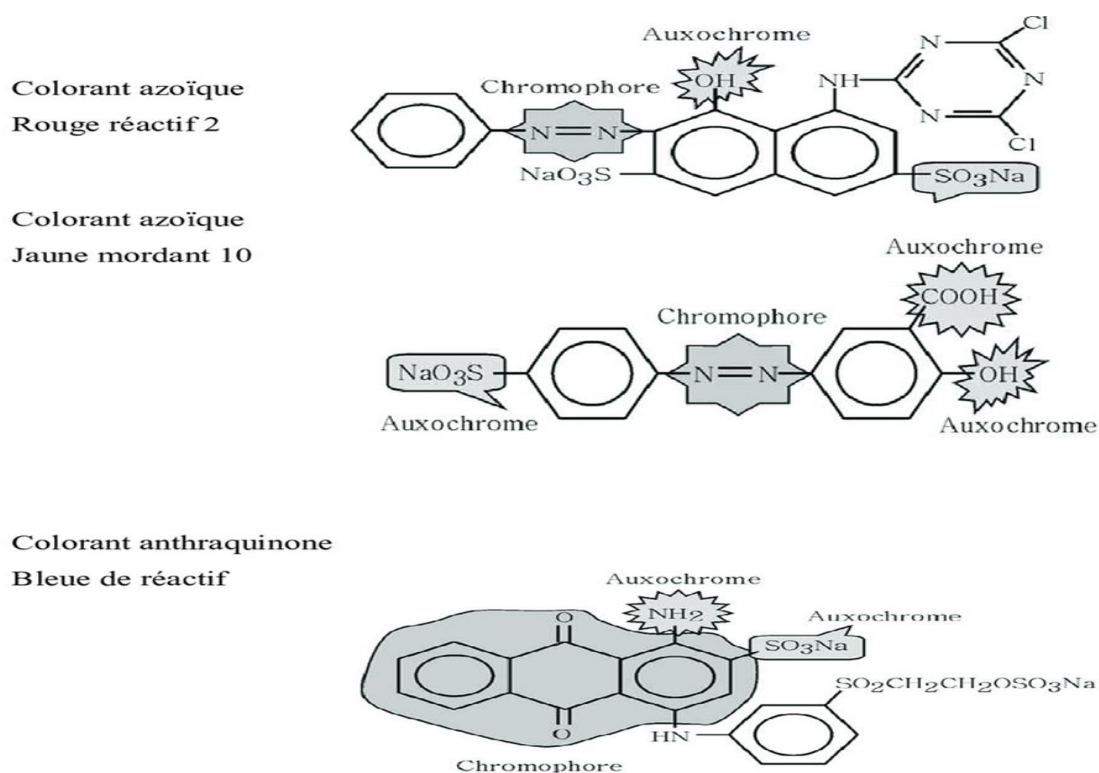
Auxochromic groups are groups of atoms comprising double non-binders. They can modify the absorption wavelength and therefore the color of the chromophore groups with which they are associated. A group is said to be auxochrome if it accentuates the effects of a chromophore group. It allows to extend towards higher wavelengths the absorption of chromophore groups therefore its presence can have an influence on the color of the chemical species.

this group can be:

- **Strong:** this is the case of amino groups  $-NH_2$  and hydroxide  $-OH$  that strongly develop the colors
- **Weak:** this is the case of the sulphonic groups  $-SO_3H$  and carboxylic  $-COOH$  which do not intervene in the coloring of the compound but solubilizes it. [5.6]

**Table I. 1:** Principle chromophoric and auxochromic groups classified by increasing intensity.

chromophore group	Auxochromic groupe
- Azo (-N=N-))	-Amino (-NH <sub>2</sub> )
-Nitroso (-N=O)	-Méthylamino (-NHCH <sub>3</sub> )
-Carbonyle (>C=O)	-Diméthylamino (-N(CH <sub>3</sub> ) <sub>2</sub> )
-Vinyle (-C=CH <sub>2</sub> ) ou méthine (>C=)	- Hydroxyle (-OH)
-Nitro (-NO <sub>2</sub> )	-Alkoxy (-OR)
-Thiocarbonyle (>C=S)	

**Figure I. 1:** Example of the chromophoric and auxochromic groups of azo dyes and anthraquinone.

#### I.1.4. Classification of colorants:

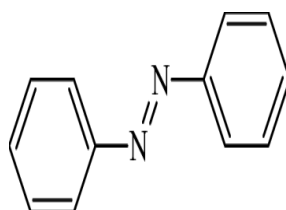
There are two ways to classify dyes, one is classified according to the properties of dyes and methods of application, and the other is classified according to the chemical composition of dyes or their characteristic groups, which is called chemical classification.

##### I.1.4.a. chemical classification

The classification of dyes according to their chemical composition depends on the nature of the chromophore group. This result in the following chemical groups:

##### *I.1.4. a.1. Azo dyes:*

Azoic refers to all the compounds that distinguish than by an azo functional group(-N=N-) That belongs to an alkyl group or an arylgroup. Azo dyes constitute the most important family in terms of application because they account more than 50% of the world production of dyes. The number of azo dyes increased and reached in the 1990's more than 10.000 molecules which were commercialized. These dyes are used in a wide range of fields: textiles, printing, food, cosmetics, and pharmaceuticals [7].

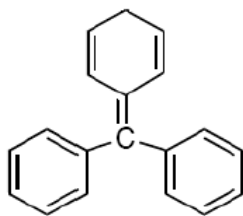


**Figure I. 2:** Azo dyes

##### *I.1.4. a.2 Triphénylméthanes dyes:*

Triphenylmethane or tritane is a hydrocarbon consisting of three phenyl rings bonded to a central carbon. We find this basic structure in a large number of colored organic compounds. Synthetic dyes have the oldest class of pigments of Triphenylmethane and its heterocyclic derivatives. Azo dyes are important from Triphenylmethane dyes because they have retained some value. Commercial, as they make it possible to cover a whole range of shades. Triphenylmethane in paper and textile mills for dyeing nylon, wool, silk and cotton. Its use is not limited to industry.

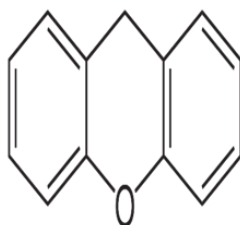




**Figure I. 3:** Triphénylméthanesdyes.

***1.1.4. a.3. Indigoïdes dyes:***

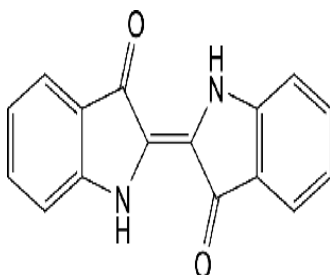
Indigo dye is an organic compound with a distinctive blue color. Indigoid pigments take their name from the indigo from which they are derived, and the isotopes of selenium, sulfur and oxygen in the indigo blue cause significant effects. It is mainly used in the production of denim fabric suitable for blue jeans and is also used as a color. Also used as a food coloring, Indigoid dyes are used as a dye in textiles, as additives in pharmaceutical products. [8, 9]



**Figure I. 4:** Indigoïdes dyes.

***1.1.4. a.4. Xanthenes dyes:***

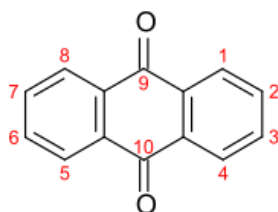
Xanthene dyes, known as fluorescein compound, are compounds that constitute the derivatives of fluorescein. It has intense brilliance halogenated. Their property as markers when of maritime accidents or flow tracers for underground rivers is despite everything well established. They are also used as a colorant in food, cosmetics, textiles and printing [10,11].  
Different type de colorants



**Figure I. 5:** Xanthenes dyes

#### ***1.1.4. a.5. Anthraquinonedyes:***

They are the second most important class of textile dyes after azo dyes from a commercial point of view. Their general formula, derived from anthracene, shows that the chromophore is a quinone ring to which hydroxyl or amino groups are attached. These products are used for coloring polyester, acetate and triacetate fibres. Cellulose. It represents 20 to 25% of the textile dye market.

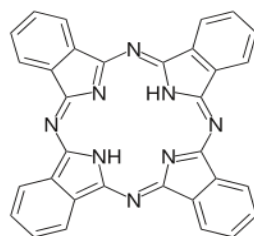


**Figure I. 6:** Anthraquinonedyes.

#### ***1.1.4. a.6. Thephthalocyanines:***

They are considered as the second most important class of textile dyes after azo dyes from a commercial point of view. Their general formula, which is derived from anthracene, shows that the chromophore is a quinone ring with a hydroxyl or an amino group. These products are used to color polyester, acetate and triacetate fibers. Cellulose accounts for 20 to 28% of the textile dye market. [12]

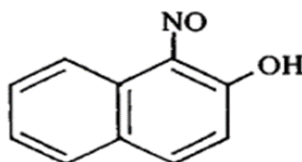
Pcs was used as dyes and pigment in the paint industry, printing, textiles and paper, due to their intense blue-green color. Since their discovery and identification in the early 20th century [13]



**Figure I. 7:** Thephthalocyanines.

***1.1.4. a.7. Nitro and nitrosated dyes:***

Due to its very moderate price, They are still used, limited in number and out dated. The simplicity of its molecular structure relates to the presence of a nitro group ( $\text{NO}_2$ ) in an orthotropic position of the electron donating group (hydroxyl or amino group).



**Figure I. 8:** Nitro and nitrosated dyes.

***1.1.4.b. Classification Tinctoriale:***

Preferably sort by fields of application If the chemical classification is of interest to the manufacturer of dyestuffs Thus, it is informed about the solubility of the dye in the dye bath, its affinity for the various fibers and the nature of the fixation This is of variable strength depending on whether the dye-substrate bond is of the ionic, hydrogen, Van der Waals or covalent type. There are different tinctorial categories defined this time by the auxochromes [14]

***1.1.4. b.1. Acid or anionic dyes:***

These dyes possess acidic groups, such as sulfonates or carboxylates that are soluble in water and are applied primarily from an acid bath. It is applied to wool, silk and nylon. When the ionic bond is established between the protonated group  $-\text{NH}_2$  of the fiber and the acidic dye group.

***1.1.4. b.2. Basic or cationic dyes:***

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper

Cationic dyes carry a positive charge in their molecule they were called basic dyes because Many of these dyes can be converted into water-insoluble dye in another meaning Basic dyes are water-soluble and yield colored cations in solution bases by addition of alkali These water-soluble cationic dyes are applied to paper, polyacrylonitrile (e.g. Dralon), modified nylons, and modified polyesters. Their original use was for silk, wool, and tannin-mordanted

cotton when brightness of shade was more important than fastness to light and washing.

The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine. Some basic dyes show biological activity and are used in medicine as antiseptics

#### ***1.1.4. b.3. Vatdyes:***

Basic dyes have been used for several decades to color cotton and other cellulose fibres despite their high cost and their muted colors, these dyes are extremely important for certain textiles because of their superior fastness. Vat dyes are insoluble dyes made soluble with reducing agents in a strongly alkaline medium; this action is called "ferment or reduce".

#### ***1.1.4. b.4. Reactivedyes:***

Approximately 80-90 % of reactivedyes are azo dyes. The other chromogenic classes are anthraquinones, dioxazines, and phthalocyanines. Reactive dyes are colored compounds that contain groups capable of forming covalent bonds between dye and substrate.

Reactive dyes form a new chemical compound when they come into contact with a fiber molecule. Reactive dyes are applied either from a solution with high pH or from neutral solutions that are later alkalized through a separate process.

It mainly comprises chromophore groups from the anthraquinones and phthalocyanic azo families [15,16].

#### ***1.1.4. b.5. Directdyes:***

Direct or substantive dyes are colored compounds that are mainly used to dye materials made from natural or regenerated cellulose (e.g., cotton, jute, viscose, or paper) in another application. It allows direct dyeing of fibers of cellulosic origin without employing mordants as auxiliaries. The essential requirement for classification of a dye in this group is its substantivity, i.e., its absorption from an aqueous salt-containing solution onto cellulosic materials. Absorption onto cotton takes place in a neutral to soda alkaline medium, and onto paper in a weakly acid to neutral medium. Because of their ease of application and moderate price, direct dyes still represent one of the largest groups of azo dyes, although their wet fastness, in particular, often only satisfies moderate requirements.

**I.1.4. b.6.Mordantdyes:**

Mordant dyes usually contain a functional ligand capable of react strongly with an aluminum, chromium, cobalt, copper, nickel or iron salt to give different colored complexes with the textile. A mordant or dye fixative is a substance used to set dyes on fabrics by forming a coordination complex with the dye. Mordants not only give the dye an affinity, but in many cases, they produce different colors and improve the fastness of a dye. There are many plants which may yield a color that is brilliant and pleasing but fades easily, unless fixed by using a mordant. There are different agencies of fading such as, light, washing, and perspiration.

**I.1.4. b.7.Dispersedyes:**

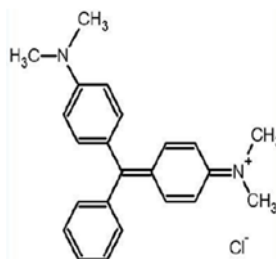
Disperse dyes are colorants with low water solubility that, in their disperse colloidal form, are suitable for dyeing and printing.

Disperse Dyes. These are substantially water-insoluble nonionic dyes for application to hydrophobic fibers from aqueous dispersion. They are used predominantly on polyester and to a lesser extent on nylon, cellulose, cellulose acetate, and acrylic fibers.

Disperse dyes are usually sold as powders, which are prepared by milling the press cake with an equal weight of a suitable auxiliary product and a little water, drying, and then mixing with diluents to give a product containing 15–40% dye. The very fine particle size ( $\leq 1 \mu\text{m}$ ) provides a large surface area that aids dissolution to allow uptake by the fibre. [5]

**I.1.5. Green of malachite:**

Malachite green is also called aniline green, benzaldehyde green, or china green is triphenylmethane dye belonging to a basic dyes class, used extensively for dyeing silk, wool and cotton. of general formula  $\text{C}_{23}\text{H}_{25}\text{ClN}_2$ .



**Figure I. 9:** Structure green of malachite.

**I.1.5. a. Use:**

Malachite green is used intensively in aquaculture. Some uses:

- Malachite green is a basic dye that has been used extensively as an antiprotozoal and antifungal medication for fish. Antimicrobial agents Fernando J. Sutili, Letícia T. Gressler, in *Aquaculture Pharmacology*, 2021
- Malachite green is soluble in water.
- It is used as an effective compound to control external fungal, bacterial, and protozoan infections of fish
- used as a treatment to control fish saprolegniosis and as a prophylactic treatment to protect fish eggs from infection.

**I.1.5.b. Toxicity of malachite green:**

This dye is used in many regions of the world because of its abundance and effectiveness. On the other hand, this dye has been banned in many countries such as America, which has not been approved by the Food Administration because of its negative impact on humans and animals, i.e. the living organism. Several studies have shown this dye to be highly toxic to freshwater fish, in both acute and chronic exposures; we give an example like rainbow trout that showed that after exposure to this dye significant developmental abnormalities in eggs, predominantly chromosome breaks, have been reported in this kind of fish therefore delayed hatching time and spinal, head, fin and tail [17].

We can devise the SYNTHETIC DYES harmful and not; for example, fibre reactive dyes like cotton, rayon, and soy it has in their structure covalent bond to the fibres. The toxicity of a dye relies on what is the composition of it in determining its structure of the dye rather than the dyeing process. The study demonstrates that the most toxic synthetic organic dyes are diazo and cationic dyes. For example, Indigo dyes have a low oral toxicity, with an LD<sub>50</sub> of 5000 mg/kg in mammals its dyes can be fatal.

**I.1.5.c. Chemical methods:**

Chemical treatments can be classified according to 2 groups: i) recovery methods which consist of precipitating, complexing or coagulating and ii) oxidation methods. Chemical oxidation is often applied for the treatment of waste water containing non-biodegradable pollutants and/or toxic and in high concentrations that other processes cannot treat or transform into biodegradable and/or non-toxic products. Thus, chemical oxidation reveals an effective process for treating wastewater.

### ***1.1.5. c.1. Photocatalysis:***

Photocatalysis is a term that dates back nearly 100 years [1,2]. The term photocatalysis derived from two words: photo related to photon and catalyst, which is a substance altering the reaction rate in its presence. In another definition, photocatalysis is defined as the change in the rate of a chemical transformation under the action of light in the presence of a catalyst which absorbs light and is involved in the chemical reaction. In this study, we use sunlight and a catalyst based on NICKEL. The solid acts catalytically, without any changes in its composition or structure, under photoirradiation, and this explanation may be consistent with most other definitions. The topic of photocatalysis as applied to the removal of trace contaminants from water has been comprehensively reviewed by S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, and W. Gemjak, Decontamination and disinfection of water by solar photocatalysis.

### **1.1.6 Physical methods:**

Various physical methods used for dye removal including adsorption, membrane filtration, ion exchange, irradiation and electrokinetic coagulation. Adsorption (on activated carbon).

- **Adsorption:**

Absorption is a very important technique in this century, Adsorption is present in many natural, physical, biological and chemical systems. The main common use of this technique in our day is purification of waters and wastewaters.

#### **1.1.6.a. Definition and general description of adsorption:**

Adsorption is the process when a molecule, or ion, called adsorbate present in a gaseous or liquid bulk sticks on the surface of a solid, rarely a liquid, called adsorbent. It is a surface process, that is, only the surface of the adsorbent is involved, and adsorbate does not diffuse into the structure of the adsorbent (in this case indeed the process is called absorption). type de adsor plus definition

Adsorption can also be defined as a physical process of separation Mixtures, the process by which one substance is disposed of by another, and in which It is concentrated in the interphase [18].

#### ***1.1.6. a .1. Type of adsorption:***

It's control in type of adsorption, a several factors Depending on the nature of the interactions that retain the adsorbate on the surface of the adsorbent, adsorption can be classified into two families: physical adsorption and chemical adsorption.

### ***1.1.6. a .2. Chemicaladsorption:***

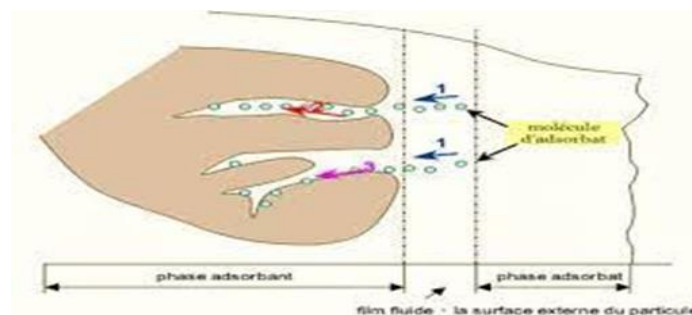
Chemisorption is a kind of adsorption which involves a chemical reaction between the adsorbate and specific surface locations on a material, known as active sites. Chemisorption, also known as Chemical adsorption, on solid materials is achieved by substantial sharing of electrons between the surface of adsorbent and adsorbate to create a covalent or ionic bond. Thus, chemical adsorption may not be fully reversible, and could require high energy for regeneration.

### **1.1.7.Physicaladsorption:**

Physical adsorption, physisorption, of molecules involves relatively weak intermolecular forces. These forces include dispersion, dipolar or Van der Waal interactions between the adsorbent surface and the adsorbate. It's a process, which attaches the target substance on a chip as a result of hydrogen bonding, van der Waals forces, electrostatic forces, and hydrophobic interactions.

#### **1.1.7.a.Description of the adsorption mechanism:**

In a way Adsorption defines the property of certain materials to fix ions or molecules (gas, metals, organic molecules, etc.) to their surface in a more or less reversible manner. There is transfer of matter from the aqueous or gaseous phase towards the solid surface.



**Figure I. 10:** Diffusion mechanism from adsorbate to adsorbent. [35]

During the adsorption of a species on a solid, the mass transfer takes place from the fluid phase towards the active sites of the adsorbent figure (1.10), involves the following steps

**\*1st stage (External diffusion):** the adsorbate diffuses through the boundary layer located around adsorbent particles.



\* **2nd stage internal diffusion (in the pores):** this is the transfer of matter into the porous structure from the outer surface of the seeds to the active sites.

\* **3rd step surface diffusion:** this is the fixing of the adsorbate on the active sites of the adsorbent.

#### ***1.1.7. a.1. Factors influencing adsorption:***

Adsorption occurs on the surface of almost all solids. The most interesting case is when the adsorption of the solute is greater than that of the solvent. So the amount adsorbed depends on many factors, the main ones being:

#### ***1.1.7. a.2. Temperature:***

The temperature leads to a considerable increase in the adsorption capacity which becomes less effective after 45°C.

#### ***1.1.7. a.3. The nature of the adsorbent:***

Depending on the polarity of adsorbents and adsorbate, the adsorption rate is different. Plus, one substance is polar, the greater its adsorption on a non-polar surface. The reduction the concentration of the adsorbate on the surface of the adsorbent results in the removal of a larger amount of adsorbate from the solution. The adsorption isotherms are established according to the equilibrium concentration between the liquid and the solid including the cumulative effects of adsorption on the total surface of the solid (external and internal).

#### ***1.1.7. b. Orientation of molecules:***

It is difficult to predict the orientation of the adsorbate molecules on the solid. this orientation depends interactions between the surface and the molecules adsorbed in solution.

#### ***1.1.7.c. Specific surface:***

The specific surface is an essential data of the characterization of solids and porous materials. The adsorbants are trying to give them a large specific area so that their quantities determine the surface that can be reached in relation to the unit of the adsorbants, knowing that the specific surface and the basic statement.

#### ***1.1.7.d. Adsorption isotherms:***

The adsorption isotherm represents the quantity adsorbed as a function of the solute concentration at equilibrium at a given temperature. The adsorption isotherm is an effective

method to understand the adsorption of surfactants on solid (skin, hair, powder–water interfaces). The adsorption isotherm is a graph that shows the surfactant concentration against the amount of surfactants adsorbed onto unit mass solid, when the solid (skin, hair, powder) is applied with a surfactant solution at a fixed temperature and reaches the equilibrium concentration.

#### ***1.1.7. d.1. Classification of adsorption isotherms:***

The shape of the isothermal curve varies according to the adsorbate – adsorbent couple studied. The adsorption isotherms of solutes with limited solubility have been classified by Gilles et al [19].

there is a relation called equilibrium isotherm provided that the experiment is carried out at constant temperature [20].

$$(y) = \frac{c_0 - c_i}{c_0} \times 100$$

C<sub>0</sub>: Initial solute concentration

C<sub>i</sub>: next concentration

- **Recovery Methods:**

**1. Clarification:** Clarification is an operation consisting in making clear a liquid which contains particles in suspension. clarification by (coagulation-flocculation-decantation) is one of the most used. It allows the elimination of suspended solids. Colloidal materials are coagulated by a supply of mineral salts (iron or aluminum). There is floc formation Chapter I: Bibliographic Synthesis Doctoral Thesis 16 which entrain the coagulated particles.

**2. Precipitation:** by adding a chemical agent makes it possible to make the chemical species insoluble to be treated which can then be recovered by filtration (Ratnaweena et al., 1992; Metcalf, 2003).

**3. Chlorination:** represents a strong oxidant and is used for water treatment or rather for disinfection such as ozone. the oxidation of organic water pollutants is carried out, and the anti-bacterial treatment, with chlorine and its oxygenated derivatives (ClO<sub>2</sub>, HClO/ClO-, HClO<sub>2</sub>/ClO<sub>2</sub>-, HClO<sub>3</sub>/ClO<sub>3</sub>-) in aqueous media. e (Sips et al., 1981).

***1.1.7.d.2 Biological Methods:***

The dyes are very stable It is not degradable naturally ,a lot of research has demonstrated the biodegradation Biological purification processes are based on the biotransformation microbial dyes.Chapitre I : Étude BibliographiqueThèse de Doctorat 17partielle ou complète des colorants par voie biologique [30,31].Microorganisms can die or reduced biodegradability Because it does not adapt with to a large number of organic pollutants, they are not always applicable on industrial effluents due to the high concentrations of pollutants .We distinguish two categories of biological treatments:

**I.1.8. Aerobic treatment:**

It is a biological wastewater treatment process that takes place in the presence of oxygen. biological unitconsisting of an activated sludge tank, the pollutants are broken down by aerobic bacteria and other microorganisms into a sludge that settles. Ideally, organic pollutants are oxidized to carbon dioxide. After purification, the sludge is separated from the wastewater by sedimentation in a decanter, part is recycled and the surplus is evacuated after pressing or centrifugation. If these techniques are adapted to a large number of organic pollutants, they are not sufficiently effective for textile waste.

It is an effective process for the treatment of waste highly loaded with COD and methane. formed can be used as heating energy. Search Unlike aerobic biodegradation, anaerobic digestion of organic compoundsIt occurs in the absence of oxygen and forms carbon dioxide, methane, and water.

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# **CHAPTER II: SYNTHESIS AND CHARACTERIZATION**

## II. Introduction

This chapter is primarily devoted to the preparation methods used for the synthesis of our materials (adsorbents), and their operating mode. Secondly, we will present the physico-chemical techniques of structural characterization used such as X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). We end with the malachite green absorption tests, where we show the operating mode and the follow-up calculation in order to determine the elimination rate of our pollutant in the presence of the synthesized adsorbents.

### II.1. Adsorbent synthesis

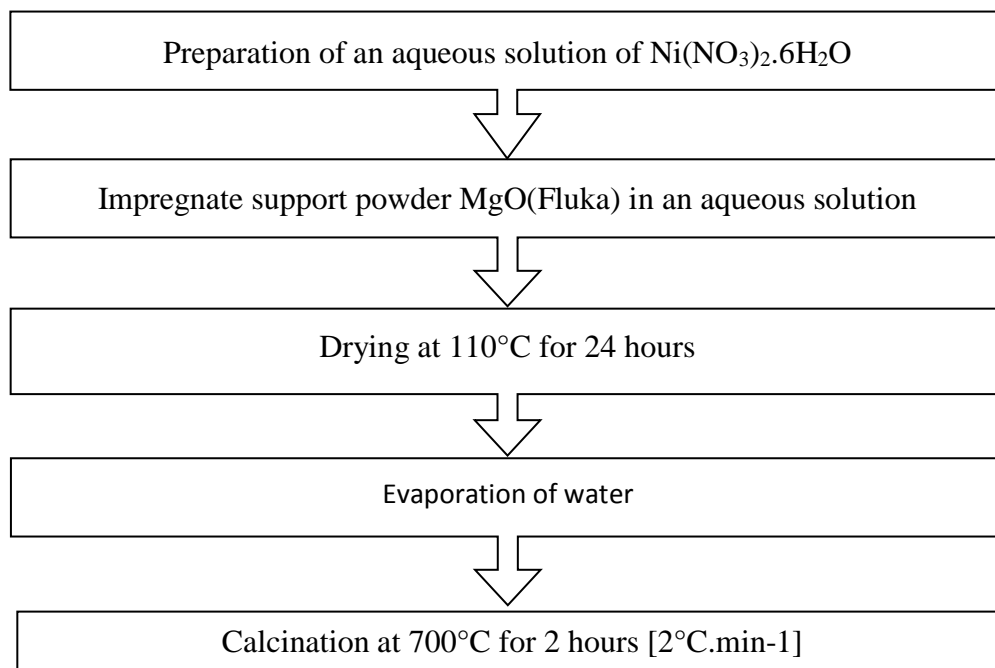
We have synthesized two adsorbents NiO-MgO by impregnation (NiO-MgO IP) and auto-combustion (NiO-MgO (AT)). The reagents used in our synthesis are in table II.1.

**Table II. 1:** Reagents used.

Reagents	Formula	Supplier
Nickel Nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Merck
Magnesium Oxide	MgO	Merck
Magnesium Nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Merck
Citrique Acide	$\text{C}_2\text{H}_5\text{NO}_2$	Panreac
Tween 80	$\text{C}_{64}\text{H}_{124}\text{O}_{26}$	Sigma

#### II.1.1. Synthesis by impregnation method:

The operating protocol, illustrated in Figure II.1, the NiO-MgO (IP) was prepared by conventional method consisting to impregnate the support powder MgO (Fluka) in an aqueous solution of metal precursors  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) with the aim to fill all the support pores. The suitable amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in the appropriate volume of bi-distilled water at 25°C. The impregnated support was then dried at 110 °C during 24 h, and calcined for 2h in air at 700°C using a ramp of 2°C.min<sup>-1</sup>.

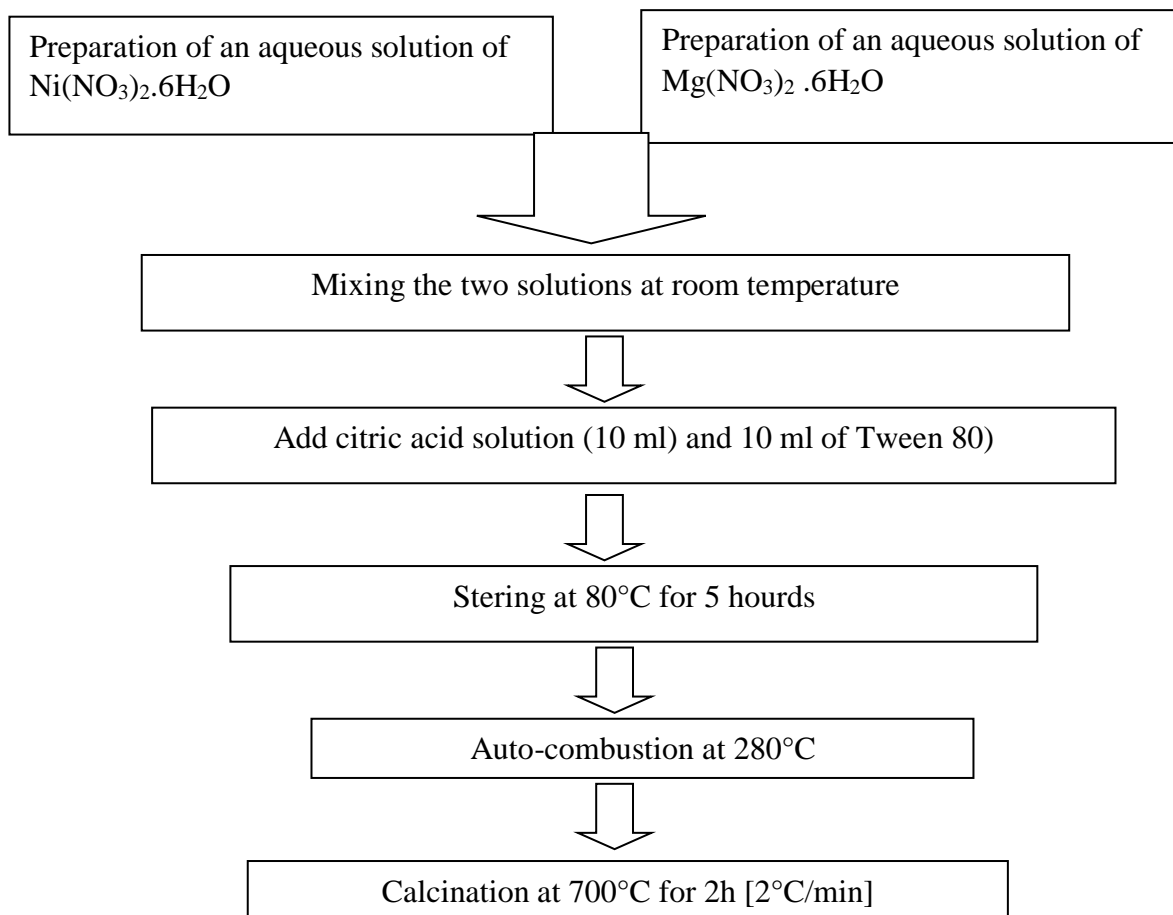


**Figure II. 1:** Preparation of NiO-MgO by impregnation (IP).

### II.1.2. Synthesis by auto-combustion method

The NiO-MgO (AT) was prepared using the Ni (NO<sub>3</sub>)<sub>2</sub>6H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O. A mixture of adequate amounts of Ni (NO<sub>3</sub>)<sub>2</sub>6H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O was dissolved in 40 ml of distilled water at 25°C. Subsequently, 10 ml of saturated solution of citrique acid C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> was added to this mixture and 10ml of surfactant tween 80 in order to increase the dispersion of nickel. The resulting solution was stirred at 80°C for 5 h and then when the temperature reached 280°C, it gave rise to the auto-combustion of the gel (exothermic reaction); the resulting solid was calcined for 2 h at 700°C. The operating protocol illustrated in Figure II.2.





**Figure II. 2:** Preparation of NiO-MgO by Auto-combustion.

## II.2. Characterization of adsorbents:

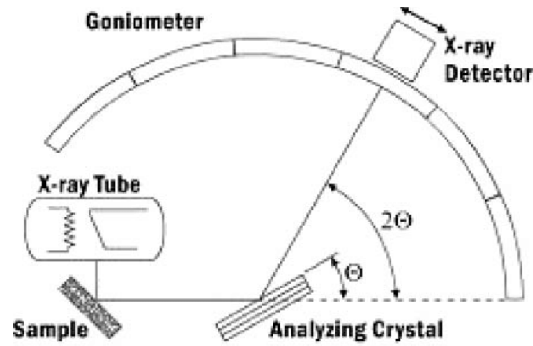
Our materials characterized by DRX and MEB analysis, in order to determine the influence of the preparation on the structures as well as on the adsorption properties of our materials.

### III.2.1 Characterization of materials by XRD

X-ray diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations, and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. A detector or counter measures the intensity of X-ray radiation diffracted in certain directions. The plot of the evolution of the intensity detected as a function of  $2\theta$  forms the diffractograms, which is characteristic of each crystalline structure [1]. The processing of the diffractograms or spectra is carried out using software based on the data from the “EVA” files.

The experimental device (Figure II.3) [2] includes:

- An X-ray source that sends X-rays to the sample.
- A goniometric circle inside which the sample is located.
- A detector connected to an amplifier.



**Figure II. 3:** Schematic diagram of a diffractometer system.

### II.2.1.1. Principle of the method:

When a polycrystalline material is subjected to monochromatic X-radiation, this radiation is diffracted by the reticular planes of the material. Each plane family gives rise to a diffraction peak for an angle  $2\theta$ , between the incident X-rays and the diffracted rays, related to the inter-reticular distance ( $d_{hkl}$ ) by Bragg's formula:

$$2d(hkl) \sin \theta = n \lambda$$

$\lambda$ : wavelength of the incident X-ray beam.

$\theta$ : Diffraction angle.

$d(hkl)$ : interreticular distance characterizing the family of planes identified by the miller indices  $h, k, l$ .

$n$  : integer.

The formula of Debye Scherrer [3] makes it possible to determine the average size of the crystallites by the following relationship:

$$D_{hkl} = (K \cdot \lambda) / \beta \cdot \cos \theta$$

Where:

$D_{hkl}$ : is the average crystallite size ( $[D] = \text{nm}$ ).

K: constant  $\approx 0.9$ .

$\lambda$ : is the wavelength of the X-ray beam.

$\theta$ : is the diffraction angle in radians

### II.2.1.2. Used device : “2D PHASER”

The study of our materials was carried out on a “2D PHASER” diffractometer (Figure II.4). The incident X-rays come from the  $K\alpha$  emission of a copper anticathode, of wavelength  $\lambda = 1.54 \text{ \AA}$ .



Figure II. 4: 2D PHASER Diffractomètre.

### II.2.2. Scanning electron microscopy (SEM)

Is a technique for observing the topography of surface, It provides information on the structure and texture of a sample.

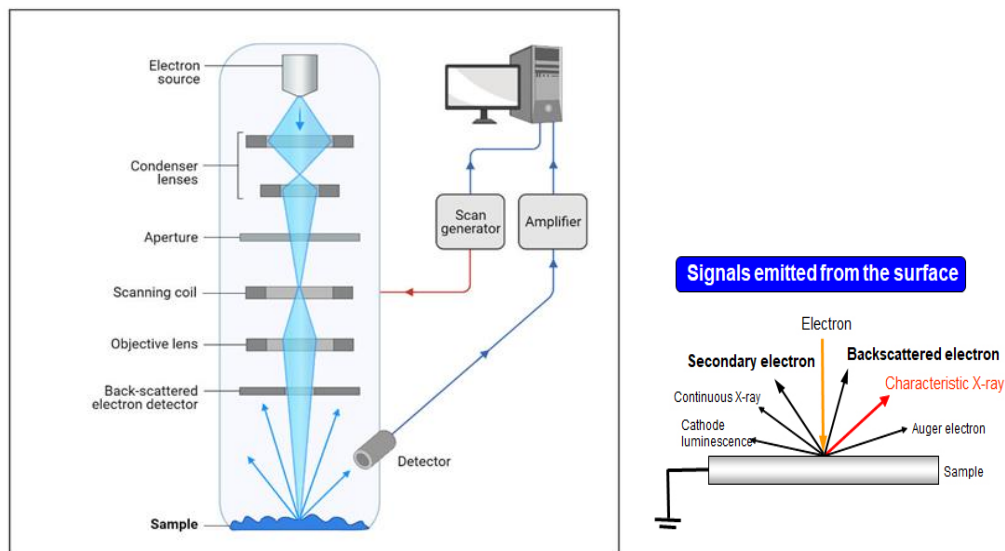
#### II.2.2.1. Principle of the method:

A beam of electrons is projected onto the sample to be analyzed. The interaction between the electron probe and the sample generates secondary, low energy electrons which are accelerated towards a secondary electron detector which amplifies the signal. Each point of impact corresponds to an electronic signal. The intensity of this electronic signal depends both on the nature of the sample at the point of impact (which determines the yield of secondary

electrons) and on the topography of the sample at the point considered. It is thus possible, by scanning the beam over the sample, to obtain a map of the scanned area [4].

A scanning electron microscope consists of an electron source, electromagnetic lenses and an electron detector (Figure II.5). When an electron beam is incident on a sample 03 phenomenon occurs [5, 6]:

- Backscatter phenomenon: some of the electrons are reflected on the surface of the sample (backscattered electrons).
- Tearing phenomenon: part of the electrons that will be able to tear electrons from the surface of materials (secondary electrons) to form new electrons.
- Emission phenomenon: The emission of X-rays or electrons (Auger effect) by ionized atoms.



**Figure II. 5:** Principle of operation of the SEM device [11] .

### II.2.2.2. Used device “ QUANTA 650”

The scanning electron microscope used for the analysis of our samples is of the "QUANTA 650" brand (Figure II.6) equipped with an X-ray detector and an energy device coupled to EDX. This detector makes it possible to determine the chemical composition presented in the sample. The samples are deposited on aluminum pads metallized with carbon.



**Figure II. 6:** SEM device « QUANTA 650 ».

### II.3. Adsorption Tests

All extraction experiments were performed in carried out in a 500ml beaker, where samples of 0.1mg of adsorbent are brought into contact with aqueous dye solutions of 200 ml volume, at a given pH. The mixture is subjected to mechanical agitation of approximately 200 rpm and samples of the aqueous phase were performed as a function of time for the determination of the adsorption yield (%). These samples are analyzed by Ultra-Violet-Visible spectroscopy with a wavelength  $\lambda_{\max} = 619$  nm.

In this study, we tried to optimize the following parameters:

- The pH of the aqueous solution.
- The initial dye concentration
- The mass of the adsorbent.

#### II.3.1. Absorbance rate calculation :

The determination of the residual concentration of the dye is carried out thanks to a analysis using a double-beam Ultraviolet-Visible Spectrophotometer “UV-2300” at the wavelength 619 nm. The **yield (y)** of adsorption is determined by the following relationship:

$$(y) = \frac{c_0 - c_i}{c_0} \times 100$$

$C_0$ : Initial concentration of malachite green

$C_i$  : concentration of malachite green at  $t_i$ (time)

Ultraviolet / visible spectrophotometry is a quantitative analysis technique, which consists in measuring the abundance or the optical density of a given chemical substance in solution. The method is based on the Beer-Lambert law which states:

- When a substance absorbs light in the ultraviolet and visible range,

The absorbed energy causes disturbances in the electronic structure of the atoms; ions or molecules. One or more electrons use this energy to jump from one low energy level to a higher energy level. These electronic transitions are in the range of 350 to 800 nm for the visible and between 200 to 350 nm for the ultraviolet.

- A homogeneous medium crossed by the light, absorbs part of it, the different radiations constituting the incident beam are differently absorbed according to their wavelength and the radiation transmitted are then characteristic of the environment.

- Consider a monochromatic light ray of wavelength ( $\lambda$ ) passing through a medium homogeneous of thickness L. The rate of decrease in light intensity as a function of the thickness of the absorbing medium is given by the Beer-Lambert law:

$$A = \log_{10} \left( \frac{I_0}{I} \right) = \epsilon cl$$

A: Absorbance.

$\epsilon$ : molar extinction coefficient ( $\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ ).

L: Thickness of the tank (cm).

C: Molar concentration of the assayed compound ( $\text{mol} \cdot \text{L}^{-1}$ ).

$I_0$ : Initial intensity of the light passed through.

I: Intensity of transmitted light.



**Figure II. 7:** Uv device

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**CHAPTER III:**  
**RESULTS AND DISCUSSIONS**

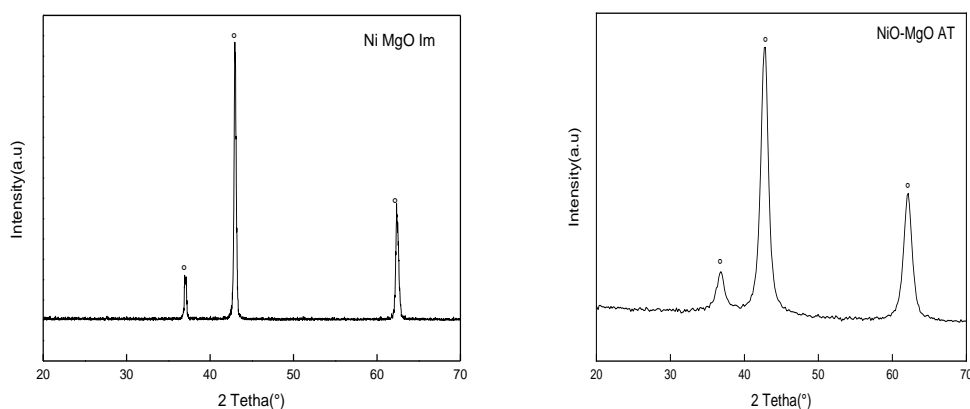
In this chapter, we give the experimental results, such as the calibration curve and the adsorption tests on NiO-MgO IP and NiO-MgO AT as well as the results of the carried out in order to determine the optimal conditions of the adsorption in our experimental conditions.

### III.1. Characterization of adsorbents :

Our materials characterized by DRX and MEB analysis, In order to determine the influence of the preparation on the structures as well as on the adsorption properties of our materials.

#### III.1.1 Characterization by XRD analysis

The X-ray diffraction patterns profiles of NiO-MgO catalysts are depicted in Figure III.1 and Table III.1. The XRD spectra show three peaks at 2theta 37.01, 42.95 and 62.21 attributed to the NiO-MgO cubic ([96-101-1174] JCPDS) and/or MgO [96-101-0096 JCPDS ] MgO solid phase.



**Figure III. 1:** XRD OF NiO-MgO prepared with different methods "NiO-MgO and MgO

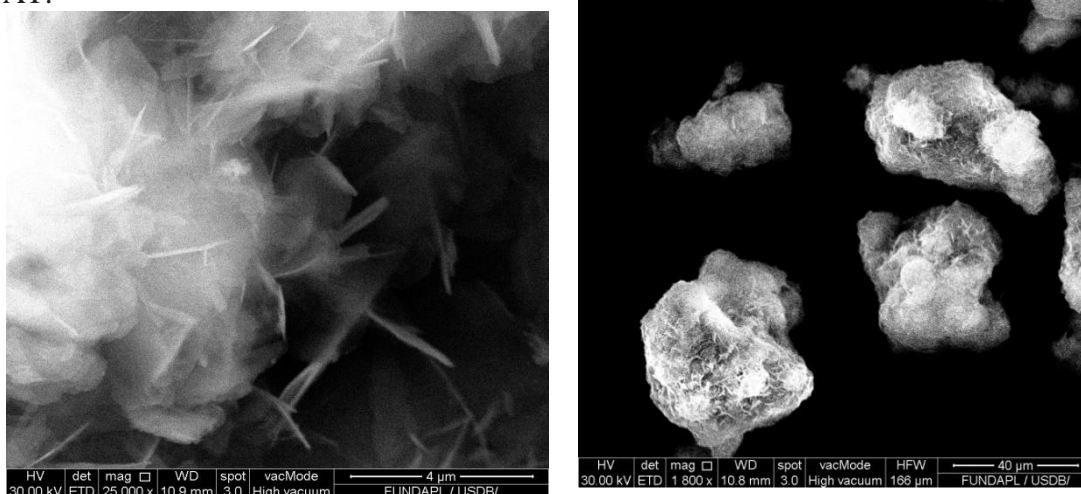
**Table III. 1:** Average crystallite size calculated by Debye Scherrer's law

Photo catalyst	Average crystallite size (nm) determined by XRD
NiO-MgO (AT)	8
NiO-MgO(IP)	28

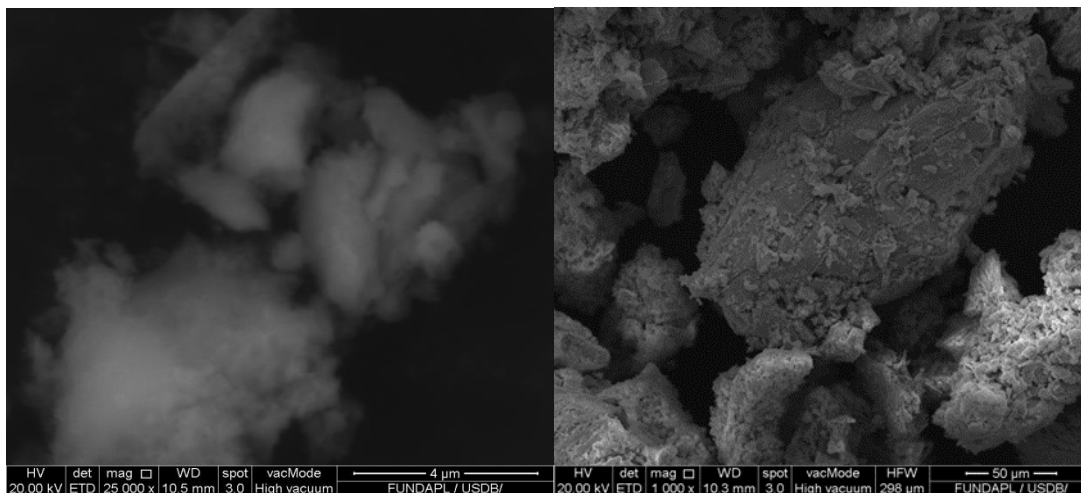
The size of the crystallites calculated by the Debye Scherrer relationship is 28 nm for the impregnation synthesis and 8 nm for the auto-combustion method. Auto-combustion method gave us the smallest crystallite size.

### III.1.2. Characterization by XRD analysis

SEM analysis results show irregular structure and spongy appearance in case of NiO-MgO AT.



**Figure III. 2:** SEM Image of NiO MgO IP Material.



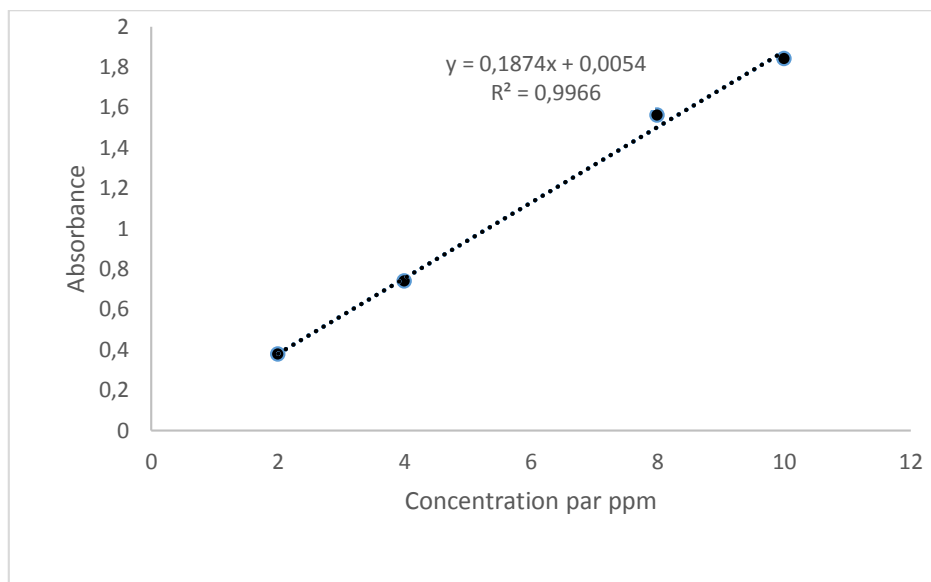
**Figure III. 3:** SEM image of NiO-MgO AT.

### III.2. Application of NiO-MgO in the elimination of Malachite green (MG)

The aim of this part is to optimize the conditions of adsorption of Malachite green by NiO-MgO (IP, AT). We study the influence of the following parameters on the adsorption of malachite green such as preparation method of adsorbent, the pH of dye, the initial concentration of pollutant and the adsorbent mass.

### III.1. Establishment of the calibration curves of Malachite green(MG)

Figure III.1 shows the malachite green calibration curve. This curve illustrates that the linearity is respected therefore this domain of concentration, the Beer-Lambert law is respected. We obtained a regression coefficient  $R^2 = 0.991$ , which represents a very good linear fit.

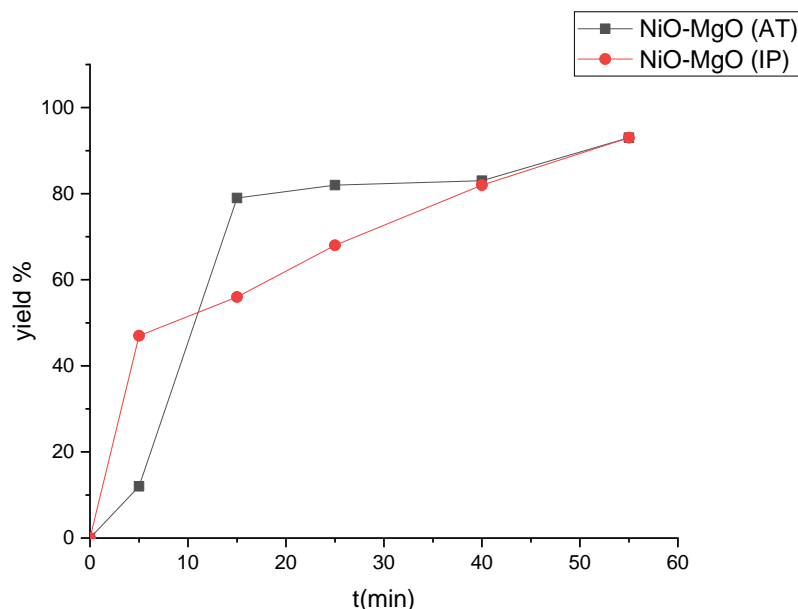


**Figure III. 4:** Malachite green calibration curve

### III.2. Adsorption tests of malachite green

#### III.2.1. Influence of the adsorbent preparation method on the adsorption of Malachite green

The results of this study are given on Figure III.1 and Table III.1



**Figure III. 5:** Effect of NiO-MgO preparation method on MG adsorption  
(pH=7, T=25°C, C<sub>0</sub> =10ppm, m = 0.02g)

**Table III. 2:** Yield variation as a function of time in conditions  
(pH =7, T=25°C, C<sub>0</sub> =10ppm, m = 0.02g) of green malachite.

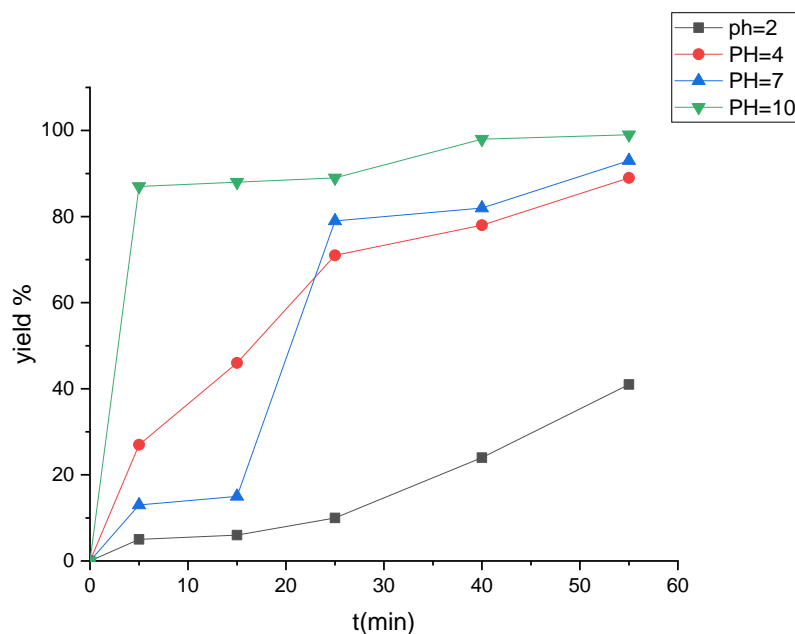
Adsorbent Time	NiO-MgO (AT)	NiO-MgO (IP)
Time (min)	Yield (%)	Yield (%)
0	0	0
5	12	47
15	79	56
25	82	68
40	83	82
55	93	93

According to the results, we notice that the adsorption is more important and faster with NiO-MgO (AT), yields of (47%, 79 %) obtained after (5min, 15min) compared to (12%, 56%) respectively in NiO-MgO IP. Knowing that the specific surface is a very important parameter in the adsorption and that it is inversely proportional to the size and of the crystallite, we can conclude that this result is explained by the small size of the NiO-MgO (AT) crystallite (8nm) compared to 28nm IP. We also observe that the same adsorption, 93% for each material after 55minutes.

The dye elimination of Malachite green is fast with NiO-MgO nanomaterial prepared by auto-combustion method; this one is maintained for the rest of the study.

### III.2.2 Influence pH on the adsorption of malachite green by NiO-MgO (AT)

pH is one of the most interesting factors we must study its effect on the adsorption of green of malachite. For this we set the temperature at 25°C, the initial concentration of malachite green at 10ppm, the adsorbent mass 0.2mg (NiO-MgO (AT)) and we vary the pH of our dye. The tests carried out in an acid medium (pH= 2 and PH=4), in a neutral medium (pH=7) and in a basic medium (pH= 10), the pH is adjusted by the addition of hydrochloric acid (0, 1M) or sodium hydroxide (0.1M). The results obtained are given in Figure III.2 and Table III.2.



**Figure III. 6:** Influence of pH on VM adsorption as a function of catalyst time

$m=0.02\text{mg}$ ,  $C_0=10\text{ppm}$ ,  $\text{pH}=(2/4/7/10)$

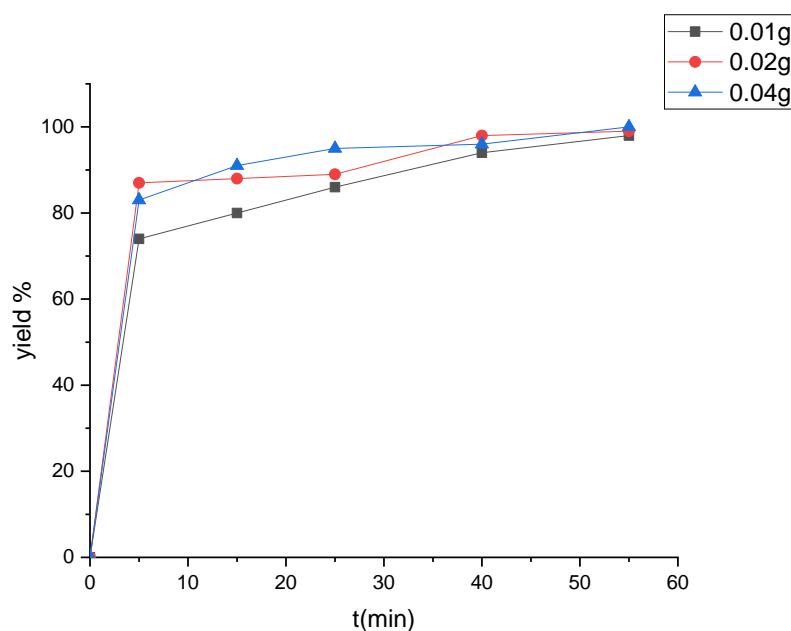
**Table III. 3:** yield variation as a function of time in conditions

$m=0.02\text{mg}$ ,  $C_0=10\text{ppm}$ ,  $\text{pH}=(2/4/7/10)$  of green malachite.

Table III. 2 pH Time	<u>pH=2</u>	<u>pH=4</u>	<u>pH=7</u>	<u>pH=10</u>
Time (min)	Yield (%)	Yeild (%)	Yeild (%)	Yeild (%)
0	0	0	0	0
5	5	27	13	<b>87</b>
15	6	46	15	<b>88</b>
25	10	71	79	<b>89</b>
40	24	78	82	<b>98</b>
55	41	89	93	<b>99</b>

The quantities of dye retained by the adsorbent from different solutions have been found in close relationship with the initial pH value of the solution. The retention rate is appreciable at basic pH. This can be explained by the fact that at low pH values, the surface of the adsorbent would also be surrounded by ions, due to the protonation of the amine functions of the malachite glass. This has the effect of decreasing the interaction of the cationic dye with the sites of the adsorbent, under the effect of repulsive forces. However, when the pH reaches the basic values ( $\text{pH} > 7$ ), the amine groups of malachite glass are deprotonated. In this case, there is an interaction between the cationic dye and the electron doublet of the nitrogen present in the group malachite glass amine.

### III.2.3. Mass influence of NiO-MgO AT on the adsorption of malachite glass



**Figure III. 7:** Influence of mass on green of malachite adsorption as a function of catalyst Time,  $C_0=10\text{ppm}$ ,  $\text{PH}=10$ ,  $m(0.01\text{g}, 0.02\text{g}, 0.04\text{g})$

In adsorption processes, determining the optimal adsorbent mass used is an important parameter, as it can affect the degradation rate of pollutants.

A series of experiments carried out by varying the amount of adsorbent: 0.01g, 0.02g and 0.04g. The Figure represents the effect of the variation in the mass of NiO-MgO (AT) on the degradation of MG.

The results obtained (Figure III.7, Table III. 4) show that the dye degradation rate increases with increasing adsorbent mass, after 55 min we have total elimination of MG ( $Y=100\%$ ) for

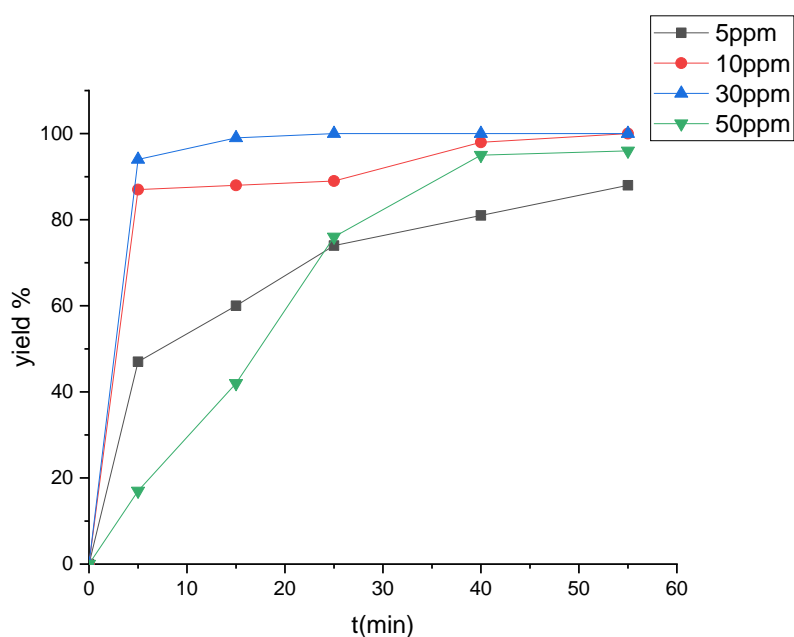
$m=0.04g, 99\%$  for  $0.02g$  and  $98\%$  with  $0.01g$ . The results show also that the MG elimination is fast with  $0.02g$  and  $0.04g$  of adsorbent, its adsorbant mass  $0.02g$  is the optimal mass in our working conditions.

**Table III. 4:** yield variation as a function of time in conditions  $C_0=10ppm$ ,  $PH=10$ ,  $m(0.01g, 0.02g, 0.04g)$  of green malachite.

$m(g)$ Time	<u><math>m=0,01</math></u>	<u><math>m=0,02</math></u>	<u><math>m=0,04</math></u>
Time (min)	Yield (%)	Yeild (%)	Yeild (%)
0	0	0	0
5	74	<u>87</u>	83
15	80	<u>88</u>	91
25	86	<u>89</u>	95
40	94	<u>98</u>	96
55	98	<u>99</u>	100

#### III.2.4. Influence of the initial concentration $C_0$ on the adsorption MG in NiO-MgO (AT)

In order to evaluate the effect of the initial concentration of malachite green on the adsorption process, we carried out experiments by varying the initial concentrations of dye by (5, 10, 30 and 50 ppm) setting the mass of NiO-MgO (AT) to  $0.02g$ . Figure III.8 reports the evolution of the adsorption activity as a function of time for the different concentrations.



**Figure III. 8:** Influence of concentration on green of malachite adsorption as a function of catalyst,  $m=0.04g, PH=10, C_0(5, 10, 30, 50)$



**Table III. 5:** Yield variation as a function of time in conditions  $m=0.04\text{g}$ ,  $\text{pH}=10$ ,  $C_0$  (5, 10,30,50) of green malachite

$C_0$ (ppm)	<u><math>C_0=5</math></u>	<u><math>C_0=10</math></u>	<u><math>m = 30</math></u>	<u><math>m=50</math></u>
Time (min)	Yield (%)	Yeild (%)	Yeild (%)	Yeild (%)
0	0	<u>0</u>	<u>0</u>	0
5	47	<u>87</u>	<u>94</u>	17
15	60	<u>88</u>	<u>99</u>	42
25	74	<u>89</u>	<u>100</u>	76
40	81	<u>98</u>	<u>100</u>	95
55	88	<u>100</u>	<u>100</u>	96

The results (Figure III.8 and Table III.5 ) show that the catalytic adsorption of MG increases with increasing initial concentration in the concentration range [5ppm-30ppm], this result can be explained by the increasing of interactions between the cationic dye and NiO-MgO. However the yield of degradation decreases with concentration with 50ppm we have yield of ( $Y = 96\%$ ) after 55min compared to 100% with concentration of 30ppm after 55min. This result can be assigned to the total occupation of active quotes, therefore the particles do not find free quotes to adsorb. We also note that the absorbance is faster with 30ppm, a yield of 100% obtained after 25min on the other hand a yield of 76% obtained with a concentration of 50ppm. We can conclude that the optimal initial concentration of MG in our experimental condition is 30ppm.

### III.3. Conclusion

Adsorption in a heterogeneous medium of malachite green in water in the presence of NiO-MgO AT gives total degradation under the following operating conditions ( $C_0= 30$  ppm,  $\text{pH}=10$ ,  $T=25^\circ\text{C}$ ,  $m=0.02$  g) after 55 min of reaction.

## Conclusion

This work falls within the context of water depollution by adsorption, the targeted pollutant is the cationic dye Malachite green, this reaction carried out in the presence of a NiO-MgO material prepared by impregnation and autocombustion. The synthesized solids characterized by XRD and SEM analysis.

The characterization and adsorption results are below:

- The XRD spectra show three peaks at  $2\theta$  37.01, 42.95 and 62.21 attributed to the NiO-MgO cubic ([96-101-1174] JCPDS) and/or MgO [96-101-0096 JCPDS] MgO solid phase.

The size of the crystallites calculated by the Debye Scherrer relationship showed that Autocombustion method gave us the smallest crystallite size 8 nm.

- SEM analysis results show irregular structure and spongy appearance in case of NiO-MgO AT.

The study of the influence of the following parameters on the adsorption of malachite green such as preparation method of adsorbent, the pH of dye, the initial concentration of pollutant and the adsorbent mass gave these results:

- The adsorption is more important and faster with NiO-MgOAT, yields of (47%, 79 %) obtained after (5min, 15min) compared to (12%, 56%) respectively in NiO-MgO IP due to the smallest crystallite size 8 nm compared to 28nm in case of NiO-MgO AT.
- The retention rate is appreciable at basic pH (10). We had 99% of elimination dye after 55 min.
- The dye degradation rate increase with increasing adsorbent mass, after 55 min we have total elimination of MG (Y=100%) for m=0.04g, 99% for 0.02g and 98% with 0.01g.
- The catalytic adsorption of MG increases with increasing initial concentration in the concentration range [5ppm-30ppm], this result can be explained by the increasing of interactions between the cationic dye and NiO-MgO. However the yield of degradation with concentration of 50ppm was (Y = 96%) after 55min compared to 100% with concentration of 30ppm after 55min.

We can conclude that the adsorption of MG in water in the presence of NiO-MgO AT gave total degradation under the following operating conditions ( $C_0= 30$  ppm, pH=10, T=25°C, m=0.02 g) after 55 min of reaction.