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The study of the degradation of organic dye by Photo-Fenton under solar irradiation

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بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

قال الله تعالى:

﴿وَقُل رَّبِّ زِدْنِي عِلْمًا ﴾

سورة طه (الآية 114)

"Thousands have lived without love ,not one without water "

W.H.Auden.

Dedication

To myself, for the courage to begin, the strength to continue, and the faith to finish.

To my beloved parents, your love has been my shelter, your sacrifices my foundation. You are my greatest blessing, and this achievement is for you.

To my dear brothers, Mohammed El Amine and Hicham, your quiet pride and protective love reminded me that I was never alone. Thank you for always standing by me.

To every soul who has loved me sincerely thank you.

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In the name of Allah, most Gracious, most Merciful.

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Table Of Contents

Liste Of Figures

Chapter I: GENERAL INFORMATION ABOUT DYES

Chapter II:

Chapter III: Materials and Analytical Techniques

Chapter IV: Results and Discussion

List Of Tables

Chapter I: GENERAL INFORMATION ABOUT DYES

Chapter II:

Chapter III

Chapter IV: Results and Discussion

List Of Abreviation

$FeSo_4$	Iron sulfate ions
H_2O_2	Hydrogen Peroxide
L	Liter
BET	Black Eriochrome T
·OH	Hydroxyl group (alcohol)
pH	Hydrogen potential
AOP	Advanced Oxidation Process
T	Temperature
TiO_2	Titanium dioxide
UV	Artificial ultraviolet light emitted by the UVlamp.
Λmax	Maximum wavelength
M	Mol/ Liter
C	Concentration
g/l	Gram per liter
$Fe(OH)_3$	Ferric hydroxide
h^+	Positive hole
C_0	initial concentration

General Introduction

General Introduction

Water is the lifeblood of humanity. It is vital for survival itself and supports the health, resilience, development and prosperity of people and planet alike. But humanity is blindly travelling a dangerous path. Vampiric overconsumption and overdevelopment, unsustainable water use, pollution and are draining humanity's lifeblood, drop by drop[1].

One of the major future challenges facing humanity is to secure the supply of clean water to the world population. It is widely proven that population growth and pollution have a negative impact on water quality. Indeed, nowadays, dyes used in industrial activities are increasingly becoming a problematic class of pollutants to the environment. Due to the complex structure of dyes, their discharge to water bodies generates bad aesthetic and health problems (De Jesus da Silveira Neta et al., 2011). Over the last few years, several classes of dyes have been used in many industrial sectors such as rubber, textiles, cosmetics, plastics, leather, food and paper making (Kono, 2015). Wastewater discharged from these industries contains a variety of dyes and the majority of them are stable to light, heat and oxidizing agents and are usually non-biodegradable (Ngulube et al., 2017). Hence, the urgent need to remove them from the environment. Dyes can be classified as cationic, anionic, and nonionic (disperse/vat). These three kinds of dyes are the most widely used in many industries. Due to their complex structures, they are not easily biodegradable and they can therefore have destructive impacts on the environment (Kuppusamy et al., 2016).

Over the past 20 years, new treatment methods have been developed, such as advanced oxidation processes (AOPs), which have shown great success in breaking down persistent organic compounds. The objective of The full mineralization of aquatic contaminants into carbon dioxide, water, and other mineral ions is known as advanced oxidation (Saidi, 2013).

Among these techniques, the Fenton process which is based on the interaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) stands out for being straightforward, efficient, and reasonably priced.

The photo-Fenton process, a variation of this technique that uses solar irradiation, produces more hydroxyl radicals, which enhances the mineralization and degradation efficiency of organic compounds, especially when treating colorful industrial effluents[2].

In this context, our work focused on evaluating the effectiveness of the Fenton reagent and the photo-Fenton process for the degradation of black eriochrome T (BET), a dye commonly used as a model in water treatment studies.

In this thesis:

- Chapter I, provides an overview of dyes: definitions, classifications, applications and environmental impacts.
- Chapter II, deals with advanced oxidation processes (AOPs), with a particular focus on Fenton and photo-Fenton reagents used for the degradation of dyes in wastewater.
- Chapter III, describes the materials, experimental methods and analytical techniques used in this study.
- Chapter IV, is committed to the presentation and discussion of the results obtained regarding the degradation of black eriochrome t (BET) using the Fenton and photo-Fenton processes. The effect of various experimental parameters on the kinetics and efficiency of the degradation is also analysed.

Finally, a general conclusion wraps up this work by summarizing the main findings and suggesting avenues for future research.

Chapter I:

GENERAL INFORMATION ABOUT DYES

Chapter I: GENERAL INFORMATION ABOUT DYES

I.1 Introduction

The art of color application to enhance our self-appearance and the world around us has been known to man since time immemorial. Historical records of the use of natural dyes extracted from vegetables, fruits, flowers, certain insects and fish dating back to 3500 BC have been found. Color is the main attraction of any fabric. No matter how excellent its constitution, if unsuitably colored it is bound to be a failure as a commercial product. Fabric was earlier being dyed with natural dyes. These however gave a limited and a dull range of colors. Besides, they showed low color fastness when exposed to washing and sunlight (Kant, 2012).

Nowadays, dyes are becoming an important class of synthetic organic compounds used in many industries, especially textiles. Consequently, they have become common industrial environmental pollutants during their synthesis and later during fibre dyeing. The large-scale production and extensive application of synthetic dyes can cause considerable environmental pollution, making it a serious public concern. Legislation on the limits of colour discharge has become increasingly rigid. There is a considerable urgent need to develop treatment methods that are effective in eliminating dyes from their waste. Physicochemical and biological methods have been studied and applied, although each has its advantages and disadvantages, with the choice being based on the wastewater characteristics, available technology and economic factors. Some industrial scale wastewater treatment systems are now available; however, these are neither fully effective for complete colour removal nor do they address water recycling [3].

I.2 Definition

A dye is a substance used to add color to an object to be dyed. This property, which results from a particular affinity between the dye and the fiber, is the source of the main difficulties encountered during treatment. Indeed, depending on the type of application and use, synthetic dyes must meet a number of criteria: resistance to abrasion, photolytic stability, resistance to chemical oxidation (particularly to detergents) and microbial attack [4]. The characteristics specific to organic dyes increase their persistence in the environment and make them unlikely to biodegrade [5].

I.3 Nature of Dyes

I.3.1 Synthetic dyes

A dye is defined as a product capable of coloring a substance in a lasting manner. It has groups that give it its color, called chromophores, and groups that enable it to bind, called auxochromes.

I.3.2 Natural dyes

Here are few natural dyes, while there are thousands of synthetic dyes. Natural dyes are extracted from plants, trees, lichens or insects and molluscs. Yellow dyes are the most numerous. We meet two categories of natural dyes: mordant dyes and vat dyes, only the former are poorly soluble in water Classification of Dyes [6].

I.4 Dye sources and structure

Dyes have been used as colour agents in textile, leather, paper, plastic, rubber, painting, cosmetic, food and pharmaceutical industries for centuries. The majority of natural dyes are extracted from plants and mineral sources (Shahid et al. 2013). Upon the introduction of industrial revolution, the industrial activities were increased dramatically and thus natural dyes production did not meet the industrial demand. synthetic dyes production have been increased significantly.

A dye can generally be described as a coloured substance that has an affinity for the substrate to which it is being applied. It is a coloured because it absorbs in the visible range of the spectrum at a certain wavelength (Table I. 1).

Table I. 2 : Colors of the visible spectrum: wavelengths and frequencies intervals

Colour	Wavelength interval (nm)	Frequency interval (THz)
Red	~700 ~635	~430 ~480
Orange	~635 ~590	~480 ~510
Yellow	~590 ~560	~510 ~540
Green	~560 ~490	~540 ~610
Blue	~490 ~450	~610 ~670

The structural framework of synthetic dyes is the principal determinant of their optical properties, chemical reactivity, and environmental persistence. Most dye molecules comprise two essential components: chromophores, responsible for color through the absorption of visible light, and auxochromes, which modify color intensity and enhance dye–substrate interactions**.**

Chromophores: Chromophores are conjugated systems with unsaturated functional groups such as azo (–N=N–), carbonyl (C=O), nitro (–NO_2), or quinoid structures. These allow delocalized π electron systems to be able to absorb electromagnetic radiation within the ultraviolet-visible (UV-Vis) range (380–750 nm) and produce visible color [7].

Auxochromes: can be classified as acidic (-COOH, -OH, -SO_3H) or basic (NHR, -NR_2, -NH_2). These groups also have the important property of giving a higher affinity to the fibre. The chromogen, which is an aromatic structure (normally benzene, naphtalene or anthracene rings), is part of a chromogen-chromophore structure along with an auxochrome. (Hunger et al. 2007)

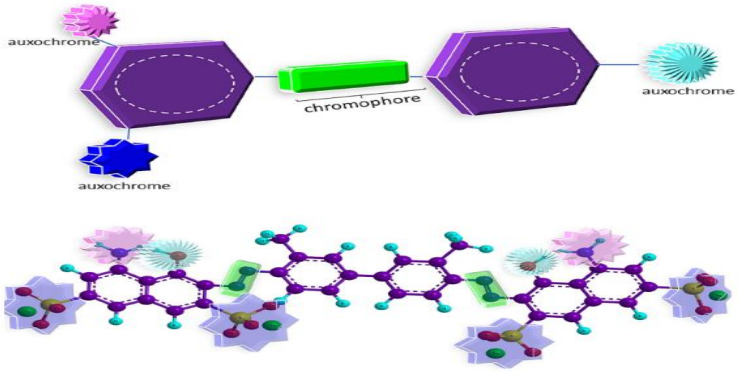

Figure I.1 : General structure of an organic dye [8].

I.5 Classification of Dyes

I.5.1 Classification based on dyeing properties

I.5.1.1 Acid or anionic dyes

Soluble in water due to their sulphonate or carboxylate groups (Figure I.2), they are so called because they allow to dye animal fibers (wool and silk) and some modified acrylic fibers (nylon, polyamide) in a slightly acid bath. The dye affinity-fiber is the result of ionic bonds between the sulfonic acid part of the dye and the groups amino of textile fibers [9] .

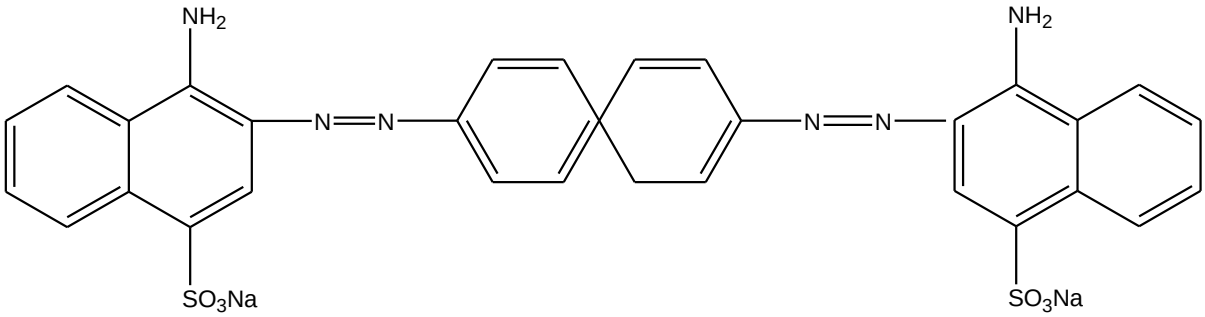

Figure I. 2 : Congo Red structure

I.5.1.2 Basic or cationic dyes

Are salts of organic amines, which gives them good solubility in water. They belong to very different chemical classes such as azodi and triphenylmethane (Figure I.3). These dyes received the name of cationic dyes, but have different structures [10] .

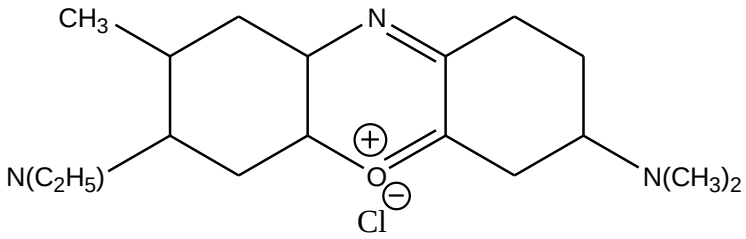

Figure I. 3 : Capri blue structure

I.5.1.3 Reactive dyes

Reactive dyes are the newest class of dyes. They owe them name to their method of attachment to the fiber. Their molecule contains a group chromophore and a reactive chemical function of triazine or vinylsulfone type ensuring the formation of a covalent bond with the fibers, they enter more and more frequently in the dyeing of cotton and possibly in that of wool and polyamides [11].

I.5.2 Classification based on chemical structure

I.5.2.1 Anthraquinone dyes

Anthraquinone compounds have long been widely used in the textile dyeing industry, especially for red dyes. These dyes are known for their water solubility, bright colors, and excellent fastness properties. The anthraquinone structure see Figure I.4 can also form linkages with azo dyes [12].

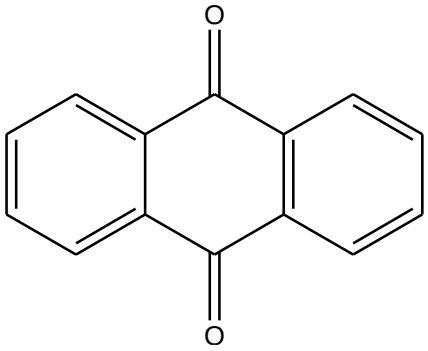

Figure I. 4: Anthraquinonie structure

I.5.2.2 Azo dyes

Azo dyes represent almost 60% of all the reactive dyes used in the textile industry followed by anthraquinone, indigoid, xanthene, arylmethane and phthalocyanine classes (Figure I. 5). (Wu et al. 2008). The color range obtained with this class of dyes is very wide (Gomes, 2001). More than one azo group can be present in the dye structure, dyes then being classified as azo, disazo, trisazo or poliazo as they have one, two, three or more groups. The anthraquinonic dyes are also widely used and comprise of a carbonyl group associated with a conjugated system of two benzene rings. As with the azo dyes, substitution groups in the aromatic rings are required to intensify the colour. The major difference is their need only of electron donors once the carbonyl groups are in the uniquely possible position to act as electron acceptors.

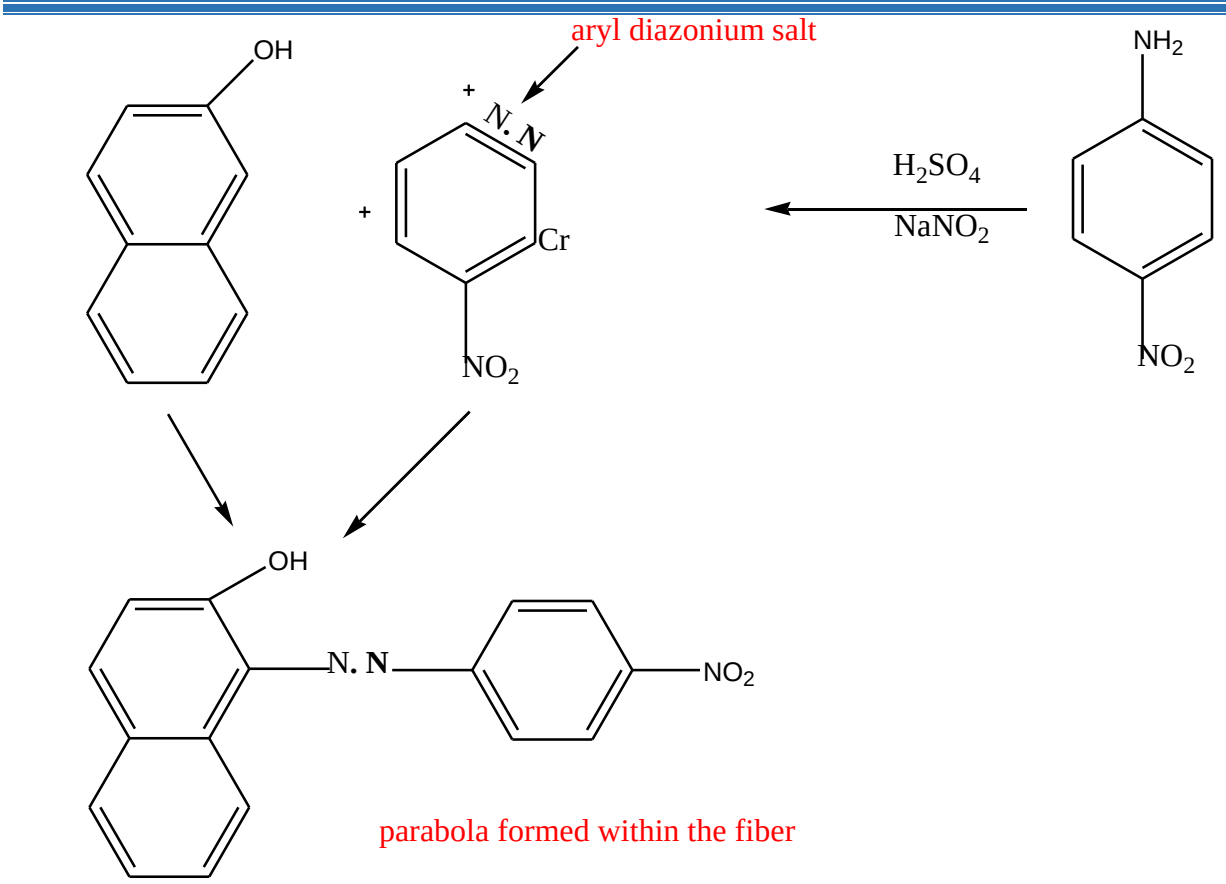

Figure I. 6 : Azo structure

I.5.2.3 Dyes of diphenylmethane and triphenylmethane

These dyes represent a much smaller category than that of azo and anthraquinone compounds. The main application is the coloring of paper for which the character of the result obtained is not a major handicap [13]**.**

I.5.2.4 Indigoids dyes

Take their name from the indigo from which they derive. Thus, the selenium, sulfur and oxygenated indigo blue cause significant hypsochromic effects with colors which can range from orange to turquoise (Figure I. 7) [14].

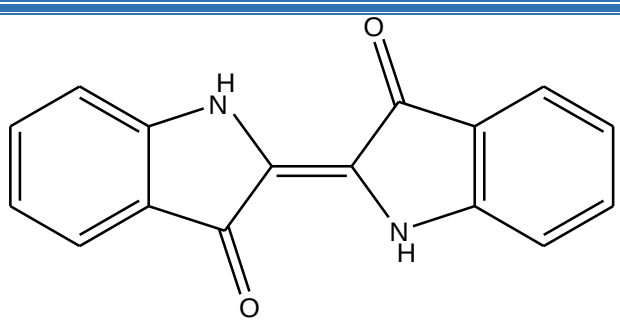

Figure I. 8 : Indigoid structure

I.5.2.5 Nitrated and nitrosated dyes

Form a very limited in number and relatively old class of dyes. They are currently still used because of their very moderate price linked to the simplicity of their structure molecular (Figure I.7), characterized by the presence of a nitro group (-NO2) in the ortho position of an electron donor group (hydroxyl or amino groups) [15].

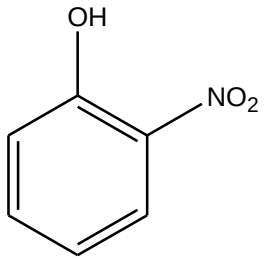

Figure I. 9 : Nitrosate structure

I.6 Applications of Dyes

The main areas of application of dyes are:

- In the textile industry of fur, leather (textile for clothing); decoration; building, transport, textile for medical use etc……
- In the plastics industry (pigments).
- In the building industry: paints (pigments).
- In the pharmaceutical industry (dyes).
- In the cosmetics industry.

- In the food industry (food colors).
- In various industries used for fuels and oils.
- In printing (ink, paper) [16].

There are many different industrial sectors that use dyes, as shown in the **Table I 2**.

Table I. 3 : Some important aspects of the applications of synthetic dyes in the service sectors and in industry[17].

Sectors	Dyes Used	Applications
Cosmetics	• The **main components used** Cosmetics in the cosmetic industry are **pigments** • although **dyes** are also used in **small quantities**. • **Over 80%** of the colorants used **are organic** • **Azo pigments** make up **morethan 60%** of the organic colorants.	Lipsticks,blushers,eye shadows, eyeliners and nail polish. Hair dyes representing almost 80% of cosmetic products in Europe.
Service providers (hospitals and universities)	• Dyes used between the sector differ depending on the process of application.	Biological staining techniques,colouration of pharmaceuticals, staining of cells and for chemotherapy process as the detection of lymph nodes, and the location of the tumor lesions.
Textile	• The textile industry **uses** a **large variety** of synthetic dyes. • **Azo dyes** are the most employed. • Textile Further, textile industry dyes are classification according to their **industrial application** as acid, basic, reactive, vat, disperse and direct dyes.	Cellulosic fibers account for the highest world textile consumption. The different dyes applied depends on properties such as affinity for the fibre, diffusion, reactivityand stability of the bond between the dye and the fibre.

I.7 Health and Environmental Impact of dyes

Approximately 40 000 different synthetic dyes and pigments are used industrially, and about 450 000 tons of dyestuffs are produced worldwide. Azo dyes are the largest and more versatile class of dyes, accounting for up to 50% of the annual production (Malik & Grohmann, 2012).

Colour is usually the first contaminant to be recognized in a wastewater because a very small amount of synthetic dyes in water (< 1 ppm) are highly visible, affecting the aesthetic merit, transparency and gas solubility of water bodies. They have a complex structure and are photo-chemically stable, they adsorb and reflect the sunlight entering water, thereby interfering with the aquatic species growth and hindering photosynthesis. Additionally, they can have acute and/or chronic effects on organisms depending on their concentration and length of exposure, thus their effects on the environment have been a matter of concern for public and environmentalist (Quan et al. 2017).

Basic dyes are water soluble and they are highly visible in water even at very low concentration. Cationic dyes such as malachite green, aniline yellow, butter yellow, basic red, basic black, turquoise reactive, neutrichrome red and methylene blue are mainly used in textile and paper industries. Basic dye bearing effluents are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer (Eren, 2009). Also, cationic dyes can cause increased in heart rate, shock, vomiting, coronary vasoconstriction, decreased cardiac output, renal blood flow and mesenteric blood flow (Leyh et al. 2003; Mahmoud et al. 2012; Shakoor and Nasar 2016).

It is reported that more than 2000 structurally different azo dyes are currently in use and up to 130 azo dyes can form carcinogenic aromatic amines during anaerobic degradation process (Khan and Malik, 2014; Yaneva and Georgieva, 2012). Human expose to anionic and azo dyes and their by-products through the digestion, skin and lungs can cause disturbance in blood formation and even DNA damage which may lead to the genesis of malignant tumors (Khan and Malik, 2014). Further, the use of direct dyes is limited and it is generally used to colour the cellulosic and protein fibres through hydrogen bonds and Van der Waals force (Chakraborty, 2014). Some of direct dyes such as direct blue 6, direct brown 95 and direct black 38 can be metabolized to benzidine which is carcinogenic to humans.The treatment of the effluents from the textile and dyestuff industries is challenging because the conventional wastewater treatment techniques are inadequate for the complete decolourization and removal of dye residues. This is due to the fact that dyes have complex aromatic molecular structures and thus they are stable and

extremely resistant towards biological or chemical processing. (Tehrani-Bagha et al., 2010; Nguyen & Juang, 2013).

I.7.1 Eutrophication:

Under the action of microorganisms, dyes release nitrates and phosphates in the natural environment. These mineral ions introduced in too large a quantity can become toxic to fish life and affect the production of drinking water. Their consumption by aquatic plants accelerates their anarchic proliferation and leads to oxygen depletion by inhibiting photosynthesis in the most deep streams and stagnant water.

I.7.2 Under-oxygenation:

When large loads of organic matter are added to the environment via occasional discharges, the natural regulatory processes can no longer compensate for bacterial oxygen consumption. Estimates that the degradation of 7 to 8 mg of organic matter by microorganisms is sufficient to consume the oxygen contained in liter of water [18].

I.7.3 Colour, turbidity, odour:

The accumulation of organic matter in watercourses leads to the appearance of bad tastes, bacterial proliferation, pestilential odors and abnormal colours. Willmott et al [19].evaluated that a coloration could be perceived by the human eye from 5×10^{-6} g/L. Apart from the unsightly appearance, coloring agents have the ability to interfere with the transmission of light in water, thus blocking the photosynthesis of aquatic plants.

I.8 Toxicity and environmental effects of Dyes

The textile industry produces large amounts of highly contaminated wastewater containing dyes, salts, chemicals, and heavy metals like lead, chromium, and arsenic. Processing 20,000 kg of textiles can generate over 3,000 liters of wastewater daily. About 40% of dyes contain carcinogenic organochlorine compounds. Dyes are persistent in the environment because of their thermal and photo-stability. Azo dyes, commonly used on cotton, are particularly resistant to conventional treatment methods, posing serious environmental and health risks [20], [21].

Textile dyes reduce sunlight penetration in water, hindering photosynthesis in algae and

aquatic plants, which disrupts the food chain and re-oxygenation of water bodies. Their persistence in the environment leads to toxic effects, accumulation in sediments and aquatic species, and potential formation of carcinogenic or mutagenic compounds [22].

I.9 Removal techniques of dyes

The treatment of textile waste, taking into account their heterogeneity of composition, will always lead to the design of a treatment chain ensuring the elimination of the various pollutants in successive stages. The first step is to eliminate the insoluble pollution by through pre-treatment (screening, grit removal, oil removal, etc.) and / or physical treatments or physicochemical ensuring a solid-liquid separation. Most depollution technics commonly involved in the second stage in the textile industries according to Barclay et al. as well as Buckley et al [23]. they can be categorized into three namely physical, biological, and chemical treatments:

I.9.1 Physical methods

I.9.1.1 Membrane filtration

Membrane filtration is one of the most important physical methods for textile dye removal from wastewater. In this method, due to the small pore size of the membrane, molecules larger than the filter pores become trapped. Microfiltration is a membrane-based phenomenon that involves the separation of dyes in the size range of 0.1–0.10 μm. In this process, the waste materials or dyes are remediated from the liquid with the help of a microporous membrane. Ultrafiltration is another membrane-basedmethod. Collivignarelli et al [24]. reported that dye color removal capabilities are acquired from wastewater with the help of ultrafiltration. The reactive black dye solution uses an ultrafiltration ceramic membrane and decolorizes the dye at different concentrations [25]. Reverse osmosis is also a membrane filtration mechanism that is used for the treatment of industrial wastewater that contains dyes.

I.9.1.2 Adsorption (on activated carbon)

Activated carbon-based adsorbents are widely studied in the field of adsorption owing to their robust chemical stability, low density, structural diversity, and suitability for field-scale[26] ,[27].applications.These unique characteristics generally originate from their internal pore morphology, surface characteristics, porosity, pore volume, chemical structure, and presence of

functional groups from their source material, including their activation.102–104 The commercial activated carbon and acti vated carbon synthesized from various waste materials are discussed in the subsequent section[28].

I.9.2 Chemical methods

I.9.2.1 Coagulation–flocculation

Chemical coagulation employing substances like potassium ferrate has been studied for its capacity to remove azo colors via concurrent oxidation and coagulation. This method has proven good success treating wastewater including Orange II's color [29], [30].

I.9.2.2 Advanced oxidation processes (AOPs)

AOPs include chemical, photochemical, and electrochemical methods (Ozcan et al., 2008). The development of these methods has been booming for about three decades. These treatment methods involve breaking down organic molecules or dyes into CO_2 and H_2O using chemical oxidants (H_2O_2, persulfate, etc.), with or without sunlight or UV light, catalysts (photocatalysis), as well as chemical, photochemical, and electrochemical Fenton processes, etc.(Josef, 2009).

I.9.3 Biological methods

I.9.3.1 Aerobic treatment

This is a biological treatment process that uses microorganisms in the presence of oxygen. Reactors known as bacterial beds are used for this purpose. They consist of an activated sludge unit where pollutants are broken down by aerobic bacteria and other microorganisms. After purification, the sludge is separated from the wastewater by sedimentation in After purification, the sludge is separated from the wastewater by sedimentation in a settling tank, part of it is recycled, and the surplus is discharged after pressing or centrifugation. This process has long been used to break down a large number of organic pollutants .It has proven effective for a certain category of textile waste (Sanir and Banerjee., 1999). Many classes of dyes, such as azo dyes, acid dyes (due to sulfonated groups), and reactive dyes, are resistant to this process (Hitz et al., 1978; Lin et al., 2002), and the decrease in coloration is mainly due to adsorption on sludge rather than degradation of the dye molecule.

I.9.3.2 Anaerobic treatment

In the absence of oxygen, the anaerobic digestion of organic compounds leads to the formation of carbon dioxide and methane fermentation, a process in which carefully selected bacterial strains convert the organic waste contained in wastewater into biogas (methane and CO2) (Amani et al., 2010; Park et al., 2001; Zajda and Aleksander-Kwaterczak., 2019). This process is highly effective in treating heavily loaded effluents characterized by relatively high COD (Weber and Wolfe., 1987). This anaerobic treatment is used in wastewater treatment plants and produces significant amounts of methane. The latter is used as an energy source, particularly for heating or lighting. Studies have shown that the reduction or even disappearance of color is not accompanied by the mineralization of dyes. However, the formation of more toxic intermediate compounds, particularly amines, has been reported in the literature (Meinck et al., 1977; Carliell et al., 1995; Bromley-Challenor et al., 2000; Chen et al., 2003).

Table I. 4 : Merits and demerits of dye wastewater treatment methods. [29] ,(USEPA, 1999 ; Mortula et al., 2011 ; Arifn eal., 2017).

Methods	**Merits**	**Demerits**
Physical Treatment		
Adsorption by activated carbon	Excellent ability to remove a wide variety of dyes. Adsorbent regeneration	Costly and expensive
Membrane Filtration	Effective for all dye type, water recovery and reuse	expensive to setup, generate concentrated sludge
Chemical methods		
Coagulation-flocculation	Cheap. Robust method. Suitable only for disperse, Sulphur and vat dye effluents.	Generation of huge amounts of concentrated sludge
Advanced oxidation processes (AOPs)	Can remove dye in unusual conditions. Good dye removal method.	Expensive. Not flexible. pH dependent.

Fenton reaction	Removes toxic, good for removal of both soluble and insoluble dyes	Iron sludge generation, long reaction time and ineffective for disperse and vat dyes.
Biological methods		
Aerobic treatment	Suitable for dyes Insoluble, partial or complete decolorization for all classes of dyes	Specific to certain dyes, Variable color removal, Large amounts of sludge generated, High energy requirements, Expensive treatment
Anaerobic treatment	Bleaches most dyes through a reduction process; the methane produced is reused as an energy source on-site	Unknown degradation products, many undegraded toxic compounds, requires large aeration tanks, longer acclimatization period

I.10 Conclusion

According to the literature, organic dyes are pollutants employed in a variety of industrial sectors, including the textile, chemical, automotive, and paper industries. Effluents contaminated with dyes provide serious issues, including long-term risks and possible hazards. Research has demonstrated that even in cases when these pollutants are not directly linked, diseases like cancer are caused by their metabolites.

Chapter II:

Advanced Oxidation Processes

II.1 Introduction

Varying amounts of dyes are released into the environment.Reducing or even eliminating these dyes is necessary given the proven toxicity of some of them. They are not destroyed by physicochemical or biological treatments, which is why new techniques have been the subject of great interest over the past two decades, as they can lead to the complete mineralization of these pollutants. These are advanced oxidation processes (AOPs).

II.2 Advanced Oxidation Processes

II.2.1 Definition

Advanced oxidation technology is one of the most environmentally friendly techniques for eliminating stubborn organic pollutants such as dyes that are difficult to handle with existing conventional procedures due to their chemical stability. Advanced oxidation procedures consist of a multitude of reaction systems that all create hydroxyl roots (attack selectivity), which is a desired characteristic in the treatment of dyes .

Advanced oxidation processes (AOPs) are efficient and successful treatment procedures for decomposing refractory compounds as well as mineralising stubborn, inhibiting, or poisonous pollutants during the last decades. The primary goal of AOP reactions is to generate very reactive oxidising agents i-e free hydroxyl radicals (HO·), which are non- selective, very reactive oxidising agents (EH=2,8) capable of degrading of dyes even the most persistent ones [30] .

The generation of hydroxyl radicals is promoted by the presence of ozone (O_3), H_2O_2, light, heterogeneous photocatalysis, or intense electron beam radiation. The initial stage in AOPs is the generation of hydroxide radicals (·OH, typically abbreviated as OH') rather than hydroxyl ions (OH-).This .OH is a powerful oxidizing/disrupting agent that, depending on the situation, can transform a complex organic chemical into CO_2 and H_2O. In the second phase of AOPs, the radicals produced in the first step react with degradable substances which are organic and inorganic and causing them to degrade further. UV, O3,H_2O_2, are commonly used in a synergistic combination to speed up 100–1000 times the production of hydroxyl radicals [31] , [32] . Any ability of oxidants to begin chemical processes is governed by its oxidation potential, or the ability of the oxidant to initiate chemical reactions i.e. the ability of the oxidants to break, destroy, or disrupt molecules.In recent years, research has demonstrated that most AOPs, including ozonation,

photocatalytic degradation, Fenton's reagent (H_2O_2 /Fe^{+2}), photo-Fenton, and moist air oxidation, have been shown to eradicate dangerous and refractory organics in waste water. Figure 4 shows AOPs with various combinations which are used to remove dyes from aqueous environments effectively [30].

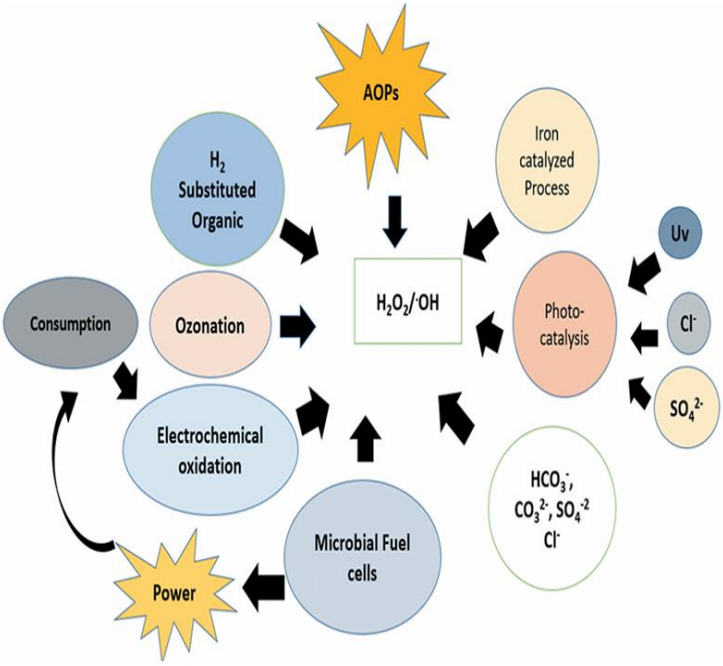

Figure II. 1 : Schematic diagrams of different divisions of AOPs.

Table II. 1 : Relative oxidation activity of common oxidants (Munter, 2001)

Oxidant	Relative oxidation activity
Hydroxyl radical	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Permanganate	1.24

II.2.2 The basic principle of AOPs

The $HO^{\bullet}$, the most oxidizing agent, known, rapidly reacts with most organic compounds with very high rate constants up to the order of 10^{11} $M^{-1}s^{-1}$. The radical can attack different organic species by radical addition/combination, electron transfer, and hydrogen abstraction. In radical

addition, according to (Eq. II.1), $HO^{\bullet}$ reacts with aliphatic and unsaturated organic compounds producing organic radicals, which are further oxidized by ferrous iron or oxygen forming stable end products. In hydrogen abstraction according to (Eq. II.2), hydrogen is removed by the generated $HO^{\bullet}$ from an organic compound forming an organic radical. This initiates a chain reaction involving the reaction between the organic radical and oxygen, producing a peroxyl radical capable of reacting with another organic compound. Electron transfer (Eq. II.3) leads to the formation of higher valent ions, where the oxidation of a monoatomic negative ion results in a free radical or atom. In the fourth route of radical recombination (Eq. II.4), two radicals combine forming a stable product (Munter, 2001).

Radical addition $R + HO^{\bullet} \rightarrow ROH$ **(Eq. II.1)**

Hydrogen abstraction: $R + HO^{\bullet} \rightarrow R\bullet + H_2O$ **(Eq. II.2)**

Electron transfer: $Rn + HO^{\bullet} \rightarrow Rn\text{-}1 + OH^-$ **(Eq. II.3)**

Radical combination: $HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$ **(Eq. II.4)** Some of the widely employed AOPs include non-photochemical (Fenton oxidation and ozonolysis) and photochemical (photo Fenton oxidation and photocatalysis) methods (Amat et al., 2014; Liu et al., 2013).

II.2.3 Advantages and drawbacks of AOPs

II.2.3.1 Advantages

A powerful treatment process like the advanced oxidation process has many advantages, but it also has its share of drawbacks (Saaidia S., 2018).

- Rapid reaction rate
- Mineralization of organic matter
- Can treat almost all organic matter and remove certain heavy metals
- Can be used for disinfection
- No sludge production, unlike chemical or biological processes
- Does not concentrate waste for further treatment

II.2.3.2 Drawbacks

- Relatively high capital and operating/maintenance costs
- Complex chemistry tailored to specific contaminants
- Removal of residual peroxide may need to be considered

II.2.4 Reactivity of hydroxyl radicals

The hydroxyl radical is one of the most powerful oxidizing agents, able to react unselectively and instantaneously with the surrounding chemicals, including organic pollutants, with rate constants of the order of 10^7 to 10^{10} $mol^{-1}.L.s^{-1}$ [32]. In particular, its reaction with alkenes and aromatic compounds is very speedy, rate constants being from of 10^9 to 10^{10} $mol^{-1}.L.s^{-1}$. This radical makes it possible to oxidise, or even mineralise, organic contaminants which are refractory to oxidation by conventional oxidants such as H_2O_2 or ozone, with reaction times of several minutes to some hours. reaction **(Eq. II.5)**

$$HO\text{-}OH \rightarrow 2HO^{\bullet} \qquad \textbf{(Eq. II.5)}$$

II.3 Classification of Advanced Oxidation Processes

In AOPs, the production of hydroxyl radicals can be realised in different ways; this can be catalytical, electrochemical and/or photochemical. In actual fact, there are several criteria of classification of AOPs. The table below presents one of the possible classifications, distinguishing photochemical processes from the rest.

Table II. 2 : Different advanced oxidation processes

Non photochemical processes	Photochemical processes
Peroxonation (O_3/H_2O_2)	UV/ H_2O_2
Fenton process (Fe^{2+}/ H_2O_2)	UV/ H_2O_2/ O_3
Sonolysis	Photo-Fenton
Radiolysis	heterogeneous photo catalysis
Electro-Fenton	Sonophotocatalysis
Electrochemical oxidation	Water catalysis in vacuum ultraviolet (UV/ H_2O)

II.3.1 Non-photochemical processes

The non-photochemical processes mentioned above can be further classed into homogeneous phase oxidation processes (Fenton process and Peroxonation), physical oxidation processes and

electrochemical processes (Electro-Fenton and Electrochemical oxidation) [31], [33].

II.3.1.1 Peroxonation (O_3 / H_2O_2)

Ozone is a powerful oxidant, but when coupled with hydrogen peroxide, the combined oxidising power (due to the production of hydroxyl radicals) may result in rapid mineralisation of organic compounds. It works well in a pH range of 7 – 8 and the optimal molar relationship O_3: H_2O_2 is 2:1 [34].

$$O_3 + H_2O_2 \rightarrow HO^{\bullet} + HO_2^{\bullet} + O_2 \qquad \textbf{(Eq. II.6)}$$

II.3.1.2 Sonochemistry

In this process, the hydroxyl radical is produced by applying a sound wave at a frequency greater than the threshold of human hearing (f > 20 kHz)

$$H_2O + \text{ultrasound (20 – 1 000 kHz)} \rightarrow HO^{\bullet} + H^{\bullet} \quad \textbf{(Eq. II.7)}$$

II.3.1.3 Radiolysis

This is the decomposition of water as a result of the absorption of energy from ionizing radiation passing through it and produces some reactive intermediates. The principal reactive intermediate is the hydroxyl radical, which exhibits oxidizing properties.

$$H_2O \rightarrow H_2O^{*} \rightarrow H^{\bullet} + OH^{\bullet} \quad \textbf{(Eq. II.8)}$$

II.3.1.4 Fe^{2+}/H_2O_2 Fenton Process

It is based on the coupling of ferrous ions with hydrogen peroxide to produce the hydroxyl radical, the ferrous ions being a catalyst:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad \textbf{(Eq. II.9)}$$

- **Factors influencing the efficiency of the Fenton process**

Several parameters governing or influencing the kinetics of the Fenton reaction were studied:

- ✓ **Optimal pH:** for the Fenton reaction, it ranges between 2.5 and 4 [35]; outside this pH range, iron complexes form, which can inhibit the reaction [36].
- ✓ **H_2O_2/Fe^{2+} ratio:** increasing the concentration of both reactants enhances the reaction kinetics, but high concentrations of the reactants can trap hydroxyl radicals [37].

- ✓ **Temperature:** increases the rate of the reactions involved in the Fenton oxidation mechanism, but it also promotes the decomposition of H_2O_2 into oxygen and water, particularly above 60°C. There is no consensus on the effect of temperature (optimal value or highest value preferred), but in general, temperatures above 60°C are not used [38].
- ✓ **Concentrations of Fenton reagents:** increasing the concentrations of Fenton reagents (Fe^{2+} and H_2O_2) leads to optimal degradation with rapid kinetics. However, an excess of these reagents negatively affects the process's efficiency. Therefore, a compromise must be found in terms of adjusting the Fe^{2+}/H_2O_2 ratio [39], [40].
- ✓ Irradiation source [41].
- ✓ Presence of hydroxyl radical scavengers (inhibitors) [42], [43].

II.3.1.5 Electrochemical Advanced Oxidation Processes

The hydroxyl radicals are generated by electrochemical means like in electro-Fenton and anodic oxidation of water.

- ✓ **Direct electrochemistry: Anodic oxidation**

Electrodes play a significant role in anodic oxidation processes as the reactions happen on or near of the surface of electrode. In the direct oxidation process, pollutants contained in the bulk of the wastewater must reach the electrode surface, and the oxidation reaction takes places once they are adsorbed onto this surface. Consequently, the nature of the electrode materials influences the selectivity and efficiency of the oxidation process and mass transfer becomes crucial to the process, and is, more often than not, the bottleneck of the oxidation rate [44].

- ✓ **Indirect electrochemistry: Electro-Fenton**

The Fenton reaction based EAOP, termed Electro-Fenton, is actively considered as the first EAOP due to the generation of hydroxyl radicals which potentially oxidizes organics. A small quantity of Fe (II) is introduced as a catalyst to an acidic solution (at pH 3) in this process to react with electro-generated H_2O_2 to produce homogeneous ·OH and Fe^{3+} ions, which is the classical Fenton reaction. [45], [46].

II.3.2 Photochemical process

These processes allow continuous and efficient hydroxyl radical production by photolysis of a solvent, generally water, and/or of an additive (H_2O_2, O_3) [47], [48], [31].

II.3.2.1 Photolysis

Photolysis is a chemical process that involves the breakage of chemical bonds in organic compounds under the influence of UV or visible light. This process usually results in the oxidation of organic compounds in water and is often used in conjunction with oxidants [49].

II.3.2.2 H_2O_2/UV photolysis (combined photolysis)

In systems where a strong oxidant is exposed to UV radiation, the principle is that energy from the light is strong enough to break the bond between molecules and thus generate radicals. Oxidants have to be photosensitive for this degradation to occur. With $\lambda < 300$ nm, the rupture of H_2O_2 is as follows;

$H_2O_2 + hv \rightarrow 2HO^{\bullet}$ **(Eq. II.10)**

II.3.2.3 Photo-Peroxonation (O_3/H_2O_2/UV)

The mechanism of this processes is in two parts; it first involves the homolysis of ozone induced by light ($\lambda < 315$ nm), to give an oxygen atom in its excited state;

$O_3 + hv \rightarrow O^* + O_2$ **(Eq. II.11)**

In aqueous solution, this oxygen atom reacts with a water molecule to give hydrogen peroxide (in gaseous phase the reaction between the oxygen atom and water directly produces a hydroxyl radical):

$O^* + H_2O \rightarrow H_2O_2$ **(Eq. II.12)**

The hydroxyl radicals can then be produced either by the decomposition of ozone by HO_2^- or the photolysis of H_2O_2:

$O_3 + HO_2^- \rightarrow HO^{\bullet} + O_2^{\bullet -} + O_2$ **(Eq. II.13)**

$H_2O_2 \rightarrow 2HO^{\bullet}$ **(Eq. II.14)**

II.3.2.4 Heterogeneous Photocatalysis

The heterogeneous photocatalysis is defined as an intersection of multidisciplinary fields of

sciences. It is based on four crucial pillars (heterogeneous catalysis, photochemistry, spectroscopy, and material sciences) figure 13. The semiconductors are activated by the light absorption with energy above its bandgap. The heterogeneous refers to the fact that the reaction is a combination between two phases liquid (the contaminants in aqueous solution) and solid (the semiconductor as powder, films or any solid state). The mainly used semiconductors are the metal oxides, the most commonly used is titanium dioxide TiO_2 because of its high chemical stability, economic cost, and the high effectiveness compared to other processes.

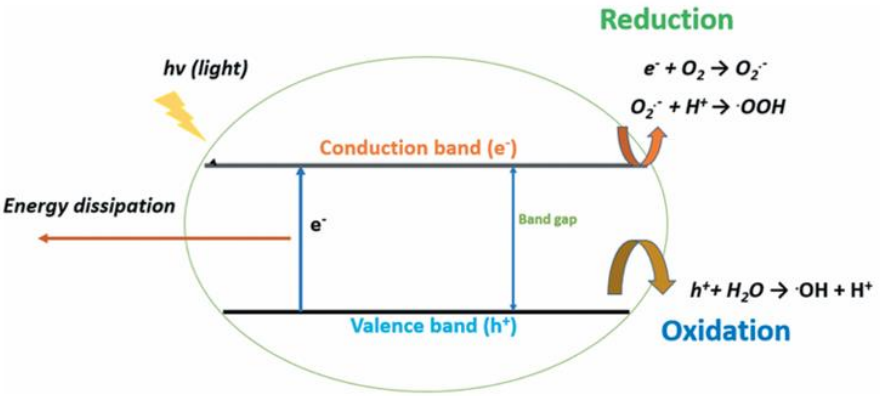

Figure II. 2 : General schematics diagram of heterogenous photocatalytic processes [50].

II.3.2.5 Sonophotocatalysis

In this case, photocatalysis and sonochemistry are used synergistically to accelerate the formation of hydroxyl radicals.

In general, POAs show great promise due to their applicability in the treatment of industrial wastewater (pharmaceutical, textile, food processing, etc.) [51], [52].

It is particularly advantageous to use these processes for the treatment of water containing a limited amount of organic matter (< 5 g/L) in order to avoid excessive reagent consumption, which would be too costly [53] . The costs to be considered for the industrial-scale development of such processes are related to both the concentration and the nature of the pollutants, the flow rate, the reactor, and the electricity consumption required to operate the lamps in the case of photochemical AOP. Little data is available in the literature on the costs of AOPs, but published results generally indicate that the total cost is comparable to water treatment processes already commonly used on a large scale.

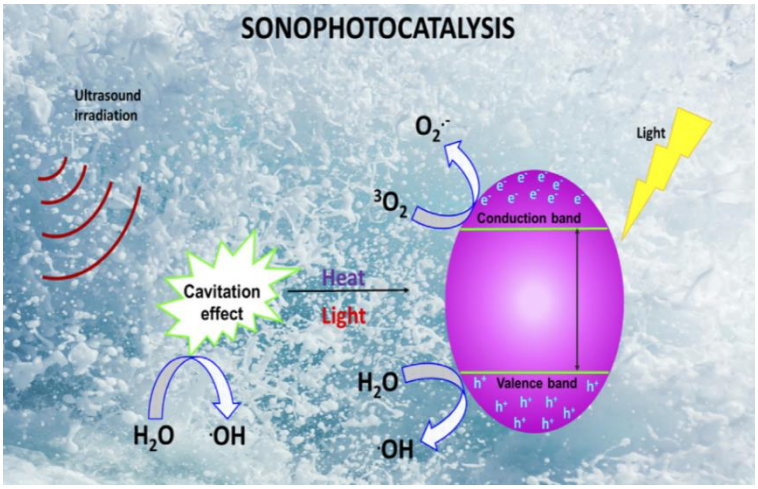

Figure II. 3 : schematic overview of a sonophotocatalytic treatment process

II.3.2.6 Water photolysis (UV/H2O)

Water absorbs light at λ < 190 nm, for this reason and vacuum being necessary in the spectrophotometers to work in this region of the optical spectrum, "Vacuum Ultraviolet" is the name given to the range of wavelengths used in water photolysis.

$H_2O + hv \rightarrow HO^{\bullet} + H^{\bullet}$ **(Eq. II.15)**

II.3.2.7 Photo-Fenton ($Fe^{2+}/H_2O_2/UV$)

The Photo-Fenton process is currently the most extensively studied, compared to the Fenton process. In fact, in the presence of UV radiation (λ > 300 nm), the efficiency of the Fenton process is greatly improved. UV irradiation (λ > 300 nm) of such a system ($Fe^{3+}/H_2O_2/UV$) generates in situ iron(II), which then immediately reacts with hydrogen peroxide to produce hydroxyl radicals, thereby regenerating iron(III) in the medium. This is referred to as the Photo-Fenton process [54] . This system has the advantage of limiting competitive reactions that consume radicals and iron(II). In the presence of hydrogen peroxide, iron(III) forms a complex in a highly acidic medium: Under the effect of photons, this complex generates iron(II) in the medium, which, by reacting with the present hydrogen peroxide, enables the production of hydroxyl radicals [55] .

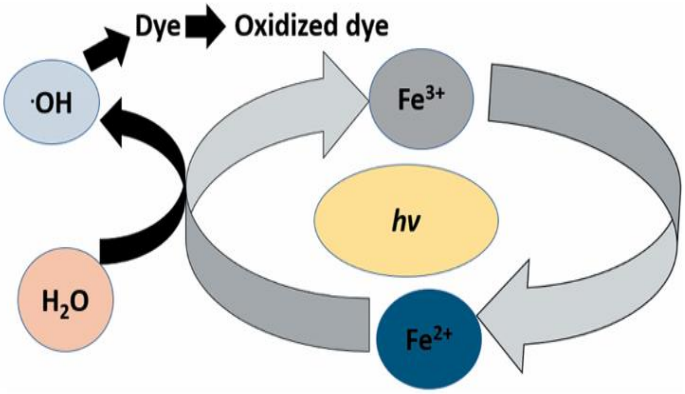

Figure II. 4 : Mechanism for the degradation of dye by photo-Fenton process.

A.Factors influencing the efficiency of the Photo -Fenton process

- **Influence of pH:**

Numerous studies on the Fenton process and related processes (photo-Fenton, electro-Fenton, etc.) have shown that a pH close to 3 appears to be the best value for optimal degradation of pollutants [56], [57].

For pH values > 4: ferric ions precipitate as iron hydroxide $Fe(OH)_3$. Since this precipitate is very stable, the reduction of Fe^{3+} to Fe^{2+} becomes very slow, and the regeneration of Fe^{2+}, as the initiator of $OH^{\bullet}$ radical production, becomes the kinetically limiting step of the process.

pH < 2 (very acidic): The reaction efficiency decreases due to three mechanisms:

ϖ Formation of ferrous complexes

ϖ Increased reaction rate of OH• scavenging by H_2O_2:

$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$ **(Eq. II.16)**

Inhibition of the ferrous ion regeneration reaction:

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ **(Eq. II.17)**

- **Effect of Temperature :**

Few studies have been conducted to evaluate the effect of temperature on the Fenton (photo-Fenton) reaction. Since temperature has a positive effect on reaction kinetics, a sufficiently high temperature is required for the oxidation reactions to occur [58] .

- **Effect of Catalyst Concentration:**

Numerous studies have shown that a high concentration of catalyst, particularly Fe^{3+}, in the solution does not lead to a higher mineralization rate. The influence of a high concentration of iron as a catalyst results in a decrease in efficiency due to the side reaction **(Eq. II.18)**between $OH^{\bullet}$ and Fe^{2+} [63].

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad \textbf{(Eq. II.19)}$$

- **Effect of Reagent Concentrations :**

The concentrations of the two reagents, as well as the ratio $R = [H_2O_2] / [Fe^{2+}]$, significantly influence the yield of the Fenton reaction. An increase in the iron concentration accelerates the reaction kinetics without affecting the yield. An increase in the H_2O_2 concentration leads to increased degradation efficiency without affecting the kinetics. An increase in the concentration of both reactants can therefore result in optimal degradation with rapid kinetics. However, a large excess of reactant can also become a limiting factor because, in this case, Fe(II) and H_2O_2 will act as traps for OH• radicals formed during the reactions (Eqs. 20–21), thereby inhibiting the oxidation of the target pollutants [59] .

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad \textbf{(Eq. II.20)}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad \textbf{(Eq. II.21)}$$

B.Advantages and disadvantages of the Photo- Fenton process

- **Advantages**

The advantages of the photo-Fenton process, beyond the Fenton reaction itself, are as follows:

- ✓ An additional supply of radicals (ferric complex Fe(OH)2+), through the photoreduction of Fe3+ ,
- ✓ the in situ production of ferrous ions that catalyze the Fenton reaction,
- ✓ a reduction in the consumption of by Fe^{2+} (side reaction) since Fe^{2+} is introduced into the reaction medium in catalytic amounts and regenerated in situ [60] . ,
- ✓ Prevention of ferric hydroxide sludge formation.

- **Disadvantages**

One of the disadvantages of this technique is the need for a continuous supply of external energy (UV radiation) from a UV lamp, which would increase the energy costs of the process. Indeed, if solar irradiation could replace the use of photochemical lamps,this would make this pollution control method very attractive and competitive for so-called emerging countries seeking inexpensive pollution control methods.

II.3.2.8 Process based on solar radiation (natural UV)

In the field of water treatment, although it is clear that early humans likely used solar energy to heat bathing water, to our knowledge, no use of solar radiation for chemical purification or disinfection of water has been reported, neither by mythologists nor by historians [61].These sources of energy (the sun) and radiation clean, abundant, inexhaustible, and free can be harnessed in the field of water treatment according to the following principle:

Solar photons are captured by substrates, causing the breaking of chemical bonds between the various constituent atoms of these molecules. Since every substance has an optimal wavelength for absorption, the solar spectrum (290–800 nm), which consists of ultraviolet (UV), visible, and infrared waves,is therefore suitable for a wide range of chemical substances, although photochemical reactions occur only in the range between 200 and 700 nm [62].

II.4 Conclusion

Dyes and other organic pollutants found in wastewater especially from the industries are harmful to the environment, aquatic life and even to human beings. In this age of ever increasing industrialism, more severe treatment methods are necessary to ensure complete destruction of these toxic elements in the wastewater released into water bodies in order to preserve life and nature.

AOPs are very attractive and promising alternatives to conventional treatment processes in regards to their efficiency as well as ability to oxidize a great variety of organic contaminants. The large number of different AOPs available is a great advantage as it presents a wide range for water treatment plants to choose from so as to suit their specifications. More research is still undergoing to ensure the cost viability of these processes on an industrial.

Chapter III:

Materials and Analytical Techniques

Chapter III: Materials and Analytical Techniques

III.1 Introduction

Conducting experimental tests requires a well-defined experimental protocol that depends on the pollutant to be removed, the chosen treatment technique, and the operating conditions that must be followed in order to achieve the desired results. In the context of this study, the oxidation of black eriochrome dye using the Fenton and photo-Fenton processes involves the use of an oxidant, a catalyst, and a light source, as well as the precise control of several reaction parameters.

This chapter provides a detailed description of the experimental methodology used for the degradation of black eriochrome using the Fenton and photo-Fenton advanced oxidation processes.

III.2 Dye data used

In this study, we focused on the investigation of the black eriochrome T (BET) dye.

III.3 Definition

The anionic azo dye (–N=N–) in organic BET is an anionic azo dye. The chemical formula is $C_{20}H_{12}N_3O_7SNa$, and the molar mass is 461.381 g/mol. In aqueous media, it is highly soluble, whereas in acetone/alcohol, it is just partially soluble. BET anionic dye molecules have good adsorption properties and have been discovered to be light and heat resistant. It's frequently utilized in the textile and chemical industries, among other things. In several chemical titrations, it is also commonly employed as an indicator. When inhaled, the BET dye causes respiratory tract difficulties as well as skin infections when it comes into touch with the skin.

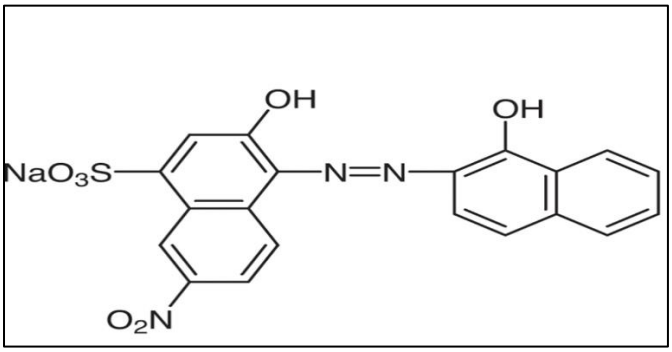

Figure III. 1 : Schematic representation of the chemical structure of black eriochrome T

III.4 Physical and chemical properties of eriochrome black T

Table III 1. *Some data on the dye studied (*eriochrome black T) [64],[65].

Eriochrome Black T	
Identification	
Name	
Name UIPAC	Sodium 4-[2-(1-hydroxynaphthalen-2-yl) hydrazin-1-ylidene] -7-nitro-3-oxo-3,4-dihydronaphthalene-1-sulfonate
Gross formula	$C_{20}H_{12}N_3O_7SNa$
Solubility	1-2g/L in water t 25° C;highly soluble in ethanol and methnol
Melting point	157-160°C
Molecular weight	461.381
PH	4.9
λmax (nm)	530

III.5 Chemicals

The chemicals used in this study are of analytical grade, the solutions were prepared using distilled water (***Table III 2.***).

Table III 2.*Chemical Reagents Used in This Study*

Reagents	Gross formula	Molecular weight	Properties and brands
Hydrogen peroxide	H_2O_2	34 ,01	Biochem 30% ; d = 1,13
Iron(II) sulfate	$FeSO_4.7H_2O$	278 ,02	Biochem
Sulfuric acid	H_2SO_4	98.078	Biochem
Methanol	CH_3OH	32	Riedel-de Haën, purity 99.7%.
eriochrome black T	$C_{20}H_{12}N_3O_7SNa$	461.381	Speciolab

III.6 Preparation of solutions

The dye used in our study is BET, supplied in the form of a powder.

III.6.1 ERIOCHROME Black T Solution

The stock solution was prepared at a concentration of 1 g L^{-1}, by dissolving the appropriate amount of dye in one liter of distilled water, with stirring to ensure complete dissolution. Working solutions were then regularly prepared from this stock solution, according to the requirements of the various experimental tests, as well as for the preparation of the calibration curve.

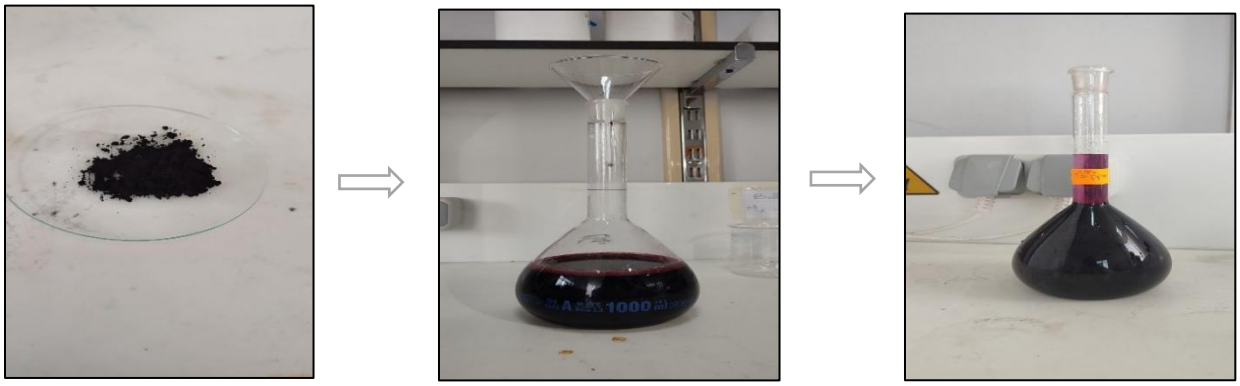

Figure III. 2 : Preparation of the eriochrome black T solution

III.6.2 Iron(II) sulfate solution

This is the catalyst used for the oxidation of the dye via the Fenton reaction. The Fe(II) solutions were prepared from a stock solution with a concentration of 10^{-2} M, obtained by dissolving a precisely determined mass (2.78 g) of $FeSO_4 \cdot 7H_2O$ in one liter of distilled water.

III.6.3 H_2O_2 Solution

The oxidizing agent used in our study is hydrogen peroxide in the form of a concentrated liquid solution with a 30% volume concentration. Specific volumes were measured from the H_2O_2 stock solution.

III.6.4 Sulfuric acid solution

To adjust the pH to a specific value, a sulfuric acid solution (H_2SO_4) was prepared at a

concentration of 1 M.

III.7 Experimental setups and procedures

III.7.1 Fenton reactor

The study of dye degradation via the Fenton process was conducted in the dark, using the setup shown in Figure II.3. This setup consists of a beaker containing the reaction mixture (colored solution, H_2O_2, Fe^{2+}), which is kept under stirring for a specified period of time. The entire system is placed in a dark chamber to prevent any light interference. Samples are taken at regular intervals. The progression of the degradation of the BET dye is monitored by measuring its concentration using a UV-Vis spectrophotometer.

The various results obtained are plotted as curves of the degradation rate = f(t)

$$\textbf{Degradation rate (\%)} = \frac{[C0]-[Ct]}{[C0]} \times \mathbf{100}$$

Where C_0 is the initial concentration of the dye, and Ct is the concentration of the dye at time t.

III.7.2 Procedure for Treatment Using the Fenton Process

The treatment of BET dye using the homogeneous Fenton process follows a simple protocol consisting of several steps. A 200 mL aqueous solution containing BET dye at a concentration of 50 mg L^{-1} is first acidified to the optimal pH using a few drops of sulfuric acid. Next, iron (II) sulfate is added to the solution at a predetermined concentration. The mixture is stirred magnetically to ensure homogenization of the solution. The radical oxidation process is initiated by the addition of hydrogen peroxide. Samples are taken at regular intervals to monitor the progression of dye degradation; each sample is treated by adding 1 mL of methanol. These samples are then analyzed by UV-Vis spectrophotometry.

III.7.3 Photo-Fenton reactor

Photodegradation experiments were performed using a photo-Fenton system (Fe^{2+}/H_2O_2 under solar irradiation) in a hermetically sealed photoreactor . The reactor was equipped with a 250 mL glass beaker mounted on a magnetic stirrer to provide continuous and uniform agitation of the reaction medium. Solar light served as the irradiation source, promoting the generation of reactive

hydroxyl radicals responsible for dye degradation. Continuous stirring ensured efficient contact between the catalyst, oxidant, and pollutant molecules during the reaction.

III.8.Analytical Techniques and Instrumentation

III.8.1 UV–Visible Spectrophotometer

An analytical tool called a UV-visible spectrophotometer is used to determine a sample's absorbance or transmittance in the ultraviolet (UV) and visible (usually 200–800 nm) portions of the electromagnetic spectrum. It measures the amount of light absorbed by a sample when light of particular wavelengths is passed through it. The Beer-Lambert law states that the absorbance and the substance's concentration are directly correlated. This method is frequently employed in water, chemical, and environmental analysis.

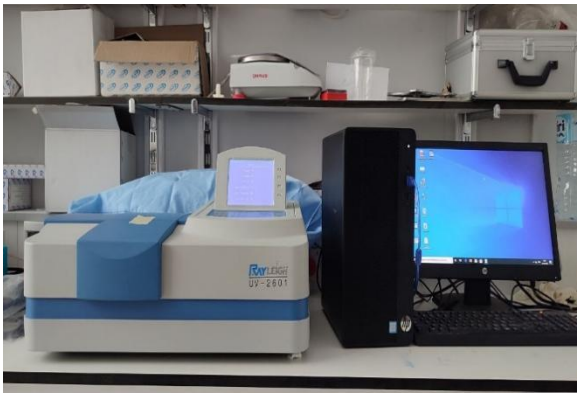

Figure III. 3 : The Spectrophotometer Rayleigh UV-2601

III.8.2 Analytical balance

Analytical balance (OHAUS): High precision (±0.1 mg) used for precise weighing.

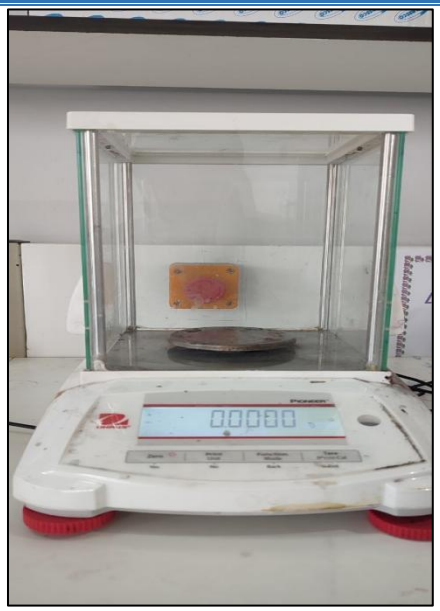

Figure III. 4 : An OHAUS analytical balance

III.8.3 PH meter (HANNA HI 5221)

The pH of the various solutions was determined using a HANNA HI 5221 microprocessor-based laboratory pH meter. The instrument was first calibrated using commercial pH 4 and 7 buffer solutions to ensure the reliability of the measurements. PH adjustment in an acidic medium was performed using sulfuric acid (H_2SO_4). Measurements were taken at room temperature (between 20 and 25 °C), taking care to rinse the electrode thoroughly between each analysis to prevent any contamination.

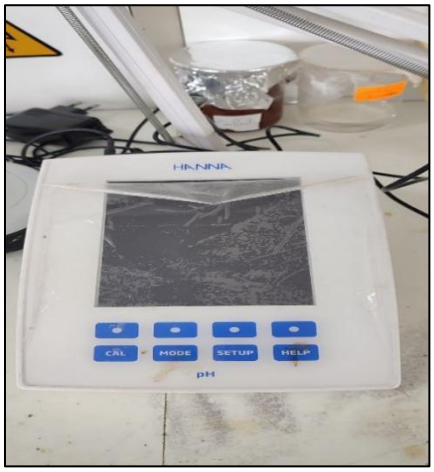

Figure III. 5 : HANNA pH meter

III.8.4 Magnetic stirrer (STUART)

A Stuart magnetic stirrer was used to ensure the homogeneity of the solutions throughout the various experimental steps. This device is equipped with a heating plate that allows for precise temperature control when required. Agitation is generated by a magnetic bar immersed in the solution, ensuring constant and efficient mixing. The rotation speed is manually adjustable, allowing the mixing intensity to be adjusted according to the requirements of each experiment.

Figure III. 6 : STUART brand magnetic stirrer

III.9 Conclusion

This chapter has outlined all the material and methodological resources used in the study of the degradation of eriochrome black T by the Fenton and Photo-Fenton processes. The attention paid to the precision of the preparations and the control of the operating conditions ensured the reliability of the experimental results.

Chapter IV:
Results and Discussion

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IV.1 Spectral Study of BET (BET)

IV.1.1 Absorption Spectrum of BET

Spectrophotometric analysis is based on the absorption of light by matter in the spectral range between 400 and 800 nm, known as the UV-Visible region.

The absorbance of the dyes is determined by spectrophotometric measurement in the visible range, based on Beer-Lambert's law.

The wavelength of the absorption maximum is 530 nm. The scan is performed using solutions of diluted concentration (20 ppm).

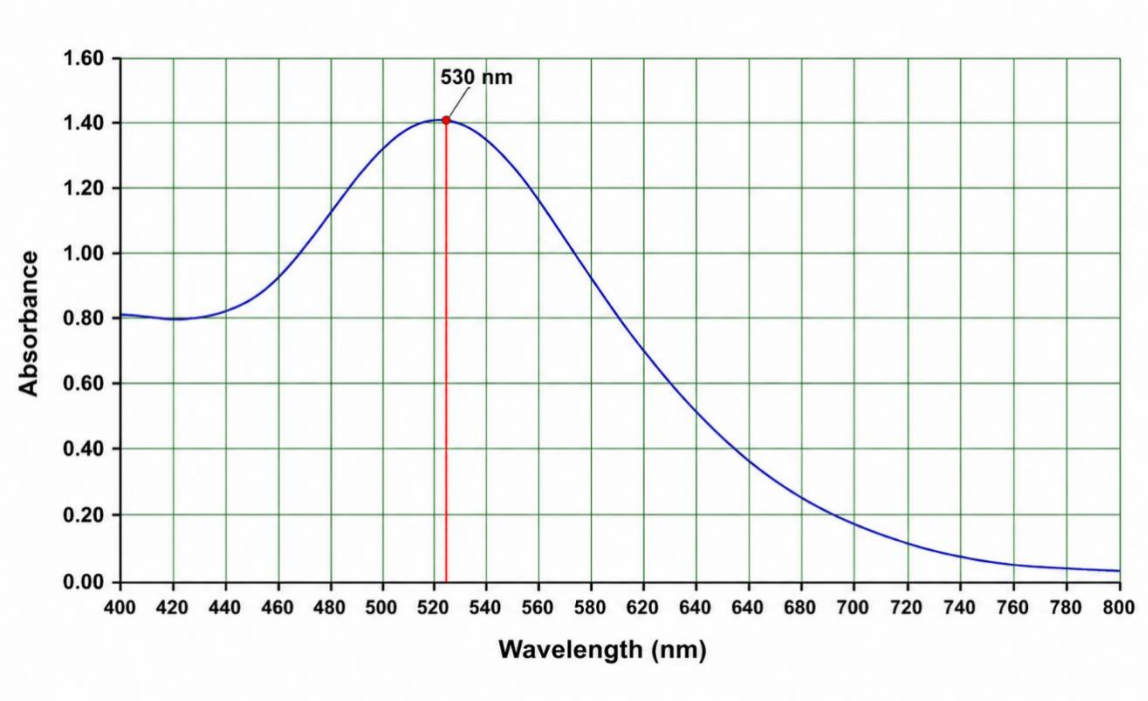

Figure IV. 1 : Maximum wavelength of the BET dye (530 nm).

IV.1.2 Absorption spectrum of H_2O_2 in the presence of Fe^{2+}

To avoid any interference caused by overlapping absorption bands, a UV-Vis spectrum was recorded for a solution containing only hydrogen peroxide and ferrous sulfate.Figure IV.2 shows that hydrogen peroxide exhibits an absorption band in the ultraviolet region, with a maximum around 210 nm. This result confirms that the absorption of hydrogen peroxide (λmax = 210 nm) does not interfere with that of the BET dye (λmax = 530 nm), as no band overlap is

observed. Absorbance measurements of the BET dye can therefore be performed without the risk of spectral overlap.

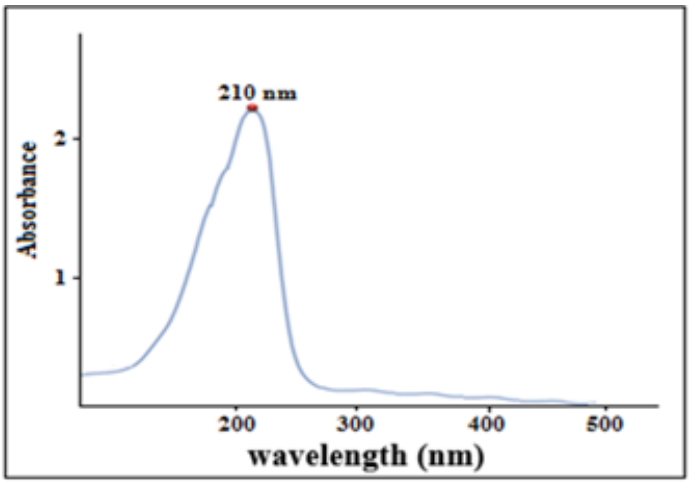

Figure IV. 2 : UV-Vis spectrum of H_2O_2 + $FeSO_4$,[H_2O_2] = 5 × 10−2 M; [$FeSO_4$] = 10−4 M at pH = 3.

IV.1.3 BET Calibration Curve

To plot the calibration curve, standard solutions were prepared with concentrations of 4, 8, 12, 16, and 20 ppm. The standard solutions were prepared from the 20 ppm BET stock solution. Absorbance measurements were taken at 530 nm. The absorbance measurement results were plotted as a calibration curve A = f(c). The calibration curve is shown in Figure (IV.3).

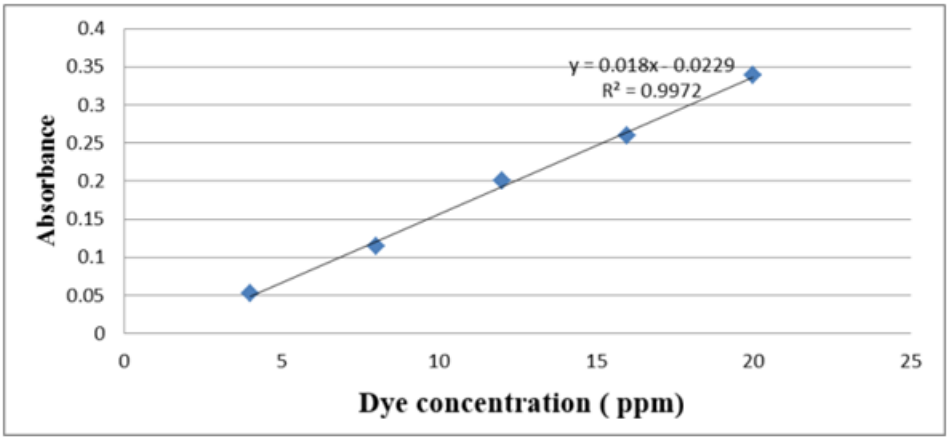

Figure IV. 3 : Calibration curve for the dye under study (BET).

IV.2 Degradation of Eriochrome Black T dye via the Fenton reaction

The Fenton process, which relies on the Fe^{2+}/H_2O_2 system, is widely used in chemical oxidation treatments to purify or pretreat wastewater in aqueous media. Under acidic conditions (pH between 3 and 4) and at room temperature, this reaction generates hydroxyl radicals (•OH), highly reactive species capable of effectively degrading organic pollutants[66]. Study of the influence of experimental parameters on the degradation of the BET dye:

IV.2.1.1 Degradation of ET in the presence and absence of Fenton reagents :

We conducted experiments both with and without Fenton reagents. The results are shown in Figure IV. 4.

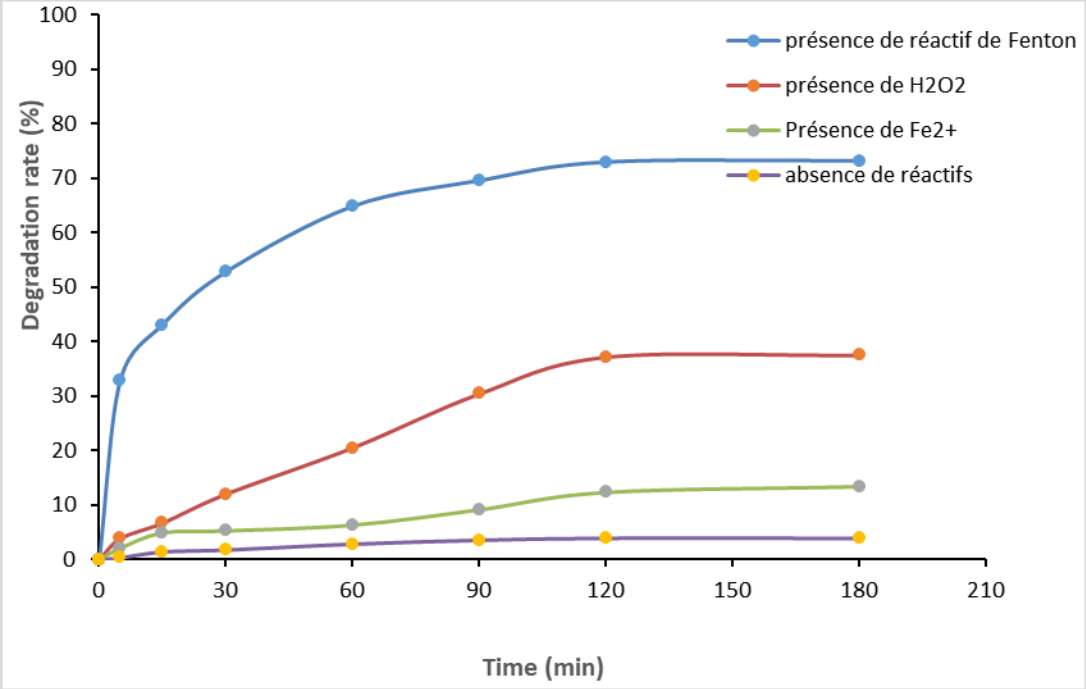

Figure IV. 5 : Rate of dye degradation in the presence and absence of Fenton's reagent.

Experimental conditions: [BET] = 50 ppm; $[Fe^{2+}] = 10^{-3}$ M; $[H_2O_2] = 5 \times 10^{-2}$ M; [pH] = 3; ƛ(max) = 530.

The graph shows the change in the degradation rate of BET over time under different experimental conditions: the presence of the Fenton reagent (Fe^{2+} + H_2O_2), the presence of hydrogen peroxide (H_2O_2) alone, ferrous iron (Fe^{2+}) alone, and the absence of reagents (control).

It is clear that the Fenton system is the most effective at degrading the dye, achieving a degradation rate of over 70% after 120 minutes. This efficiency is due to the in situ generation of hydroxyl radicals (•OH), highly reactive oxidizing species formed by the reaction between Fe^{2+} and H_2O_2 according to the following mechanism:

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-}$$

These hydroxyl radicals rapidly and non-selectively attack organic molecules, causing their oxidation and mineralization. In comparison, the degradation of BET in the presence of H_2O_2 alone is much slower and plateaus at around 35%. This shows that without a catalyst, the formation of •OH radicals is limited, although H_2O_2 can undergo self-decomposition or be weakly activated by ambient light or temperature. The curve corresponding to the presence of Fe^{2+} alone shows a low degradation rate (approximately 15%), likely due to adsorption of the dye onto the metal ions or to minor oxidation by oxygen dissolved in the medium. Finally, the blank curve (no reagents) remains virtually stable, indicating that eriochrome black t is stable in solution in the absence of any oxidizing agent, and that no significant natural or photochemical degradation occurs under these conditions. These results confirm that the H_2O_2/Fe^{2+} coupling in the Fenton process is essential for producing effective oxidizing species and ensuring rapid degradation of organic pollutants such as Black eriochrom T.

IV.2.1.2 Effect of pH :

Several studies have shown that the efficiency of the Fenton process depends heavily on the pH of the medium, as pH influences the availability of ferrous ions and the stability of hydrogen peroxide. In this study, the influence of pH was evaluated through a series of experiments conducted at pH 1, 2, 3, and 5.9, while keeping the initial concentrations of H_2O_2 and Fe^{2+} constant. The results indicate that the degradation of methylene blue is strongly affected by the acidity of the reaction medium. The degradation rate reaches its maximum at pH = 3, which corresponds to the system's optimal pH. At this value, the production of hydroxyl radicals (•OH) is maximal, promoting rapid and efficient oxidation of the dye. At lower pH values (1–2), the system's activity is reduced, likely due to the slow decomposition of H_2O_2 and the excessive stabilization of ferrous species. At higher pH values (5.9), the precipitation of iron as hydroxides reduces its catalytic availability, leading to a significant drop in process efficiency. These observations confirm that pH = 3 is the optimal condition for the Fenton-based treatment of BET.

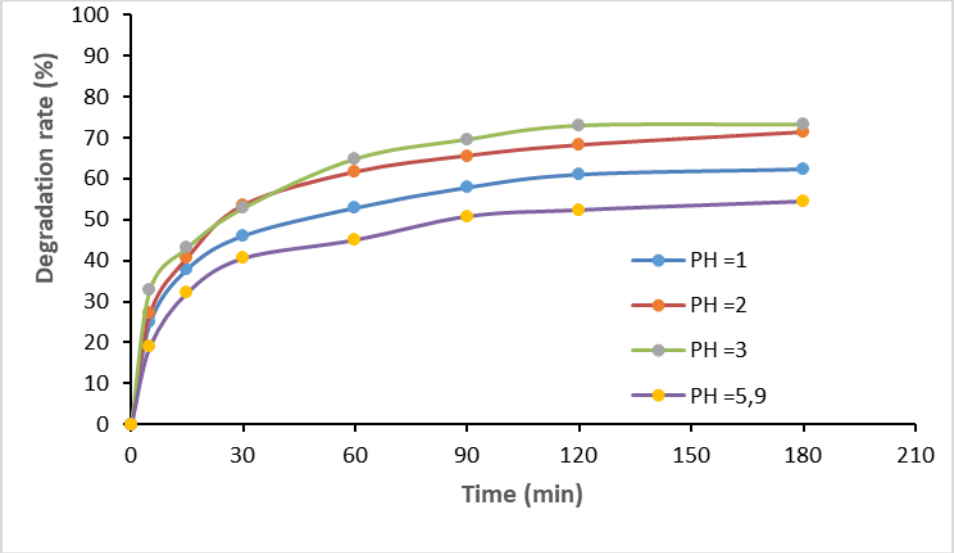

Figure IV. 6 : Effect of pH on the decolorization of BET by the Fenton process.

Experimental conditions: [BET] = 50 ppm; [Fe^{2+}] = 10^{-4} M; [H_2O_2] = 5×10^{-2} M; λ_(max) = 530 nm; t = 180 min.

Analysis of the curve shows that maximum decolorization of BET is achieved at pH = 3, with a degradation rate reaching 73%. This result is explained by optimal production of hydroxyl radicals ·OH at this acidity, facilitated by the stability and catalytic activity of Fe^{2+} ions. In a highly acidic environment (pH < 3), the process efficiency decreases due to several mechanisms: the formation of less reactive Fe^{3+}-based complexes, increased trapping of ·OH radicals by H_2O_2, and inhibition of the reduction of Fe^{3+} to Fe^{2+}. At higher pH (> 3), some of the iron precipitates as hydroxides, reducing its availability for catalysis and thus the overall efficiency of the treatment.

IV.2.1.3 Effect of hydrogen peroxide concentration:

In this study, we conducted a series of experiments at different concentrations of H_2O_2 (0.1, 0.05, 10^{-2}; 10^{-3} M) at pH = 3, with the concentrations of Fe^{2+} ions and the dye kept constant at 10^{-4} M and 50 ppm, respectively.The results of the experiments are presented in Figures IV.6

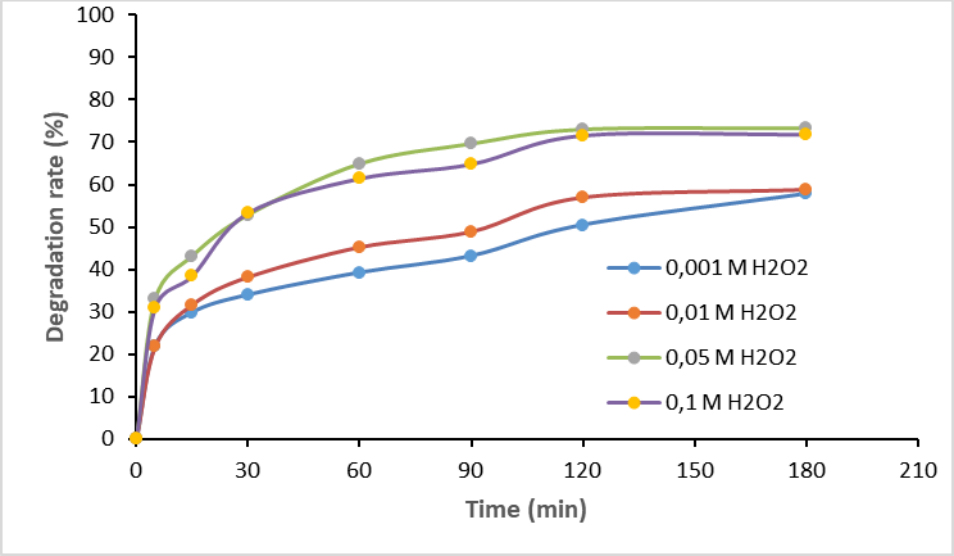

Figure IV. 7: Effect of H_2O_2 concentration on the decolorization of BET via the Fenton process.

Experimental conditions: [BET] = 50 ppm; [$FeSO_4 \cdot 7H_2O$] = 10^{-4} M; pH = 3; λ_(max) = 530 nm; t = 180 min.

Analysis of the curve shows that the rate of dye degradation increases with H_2O_2 concentration until it reaches a maximum at 0.05 M, where degradation efficiency is optimal, exceeding 70% after 120 minutes. This improvement is due to the increased production of hydroxyl radicals (•OH), the primary oxidizing agents in the process. However, beyond this concentration, as at 0.1 M, the efficiency decreases slightly. This phenomenon is explained by an excess of H_2O_2, which acts as a trap for •OH radicals, reducing their availability to attack the dye, according to the reaction:

$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$.

Thus, too low a concentration generates few radicals, while too high a concentration consumes them unnecessarily, highlighting the existence of an optimal H_2O_2 concentration to maximize pollutant degradation.

IV.2.1.4 Effect of Fe^{2+} catalyst concentration:

Another series of experiments was conducted at different Fe^{2+} ion concentrations: 0.001, 0.0001, 5.10^5, and 0.00001 M at pH = 3, with the concentrations of hydrogen peroxide and dye kept constant at 0.05 M and 50 ppm, respectively. The results are shown in the figure

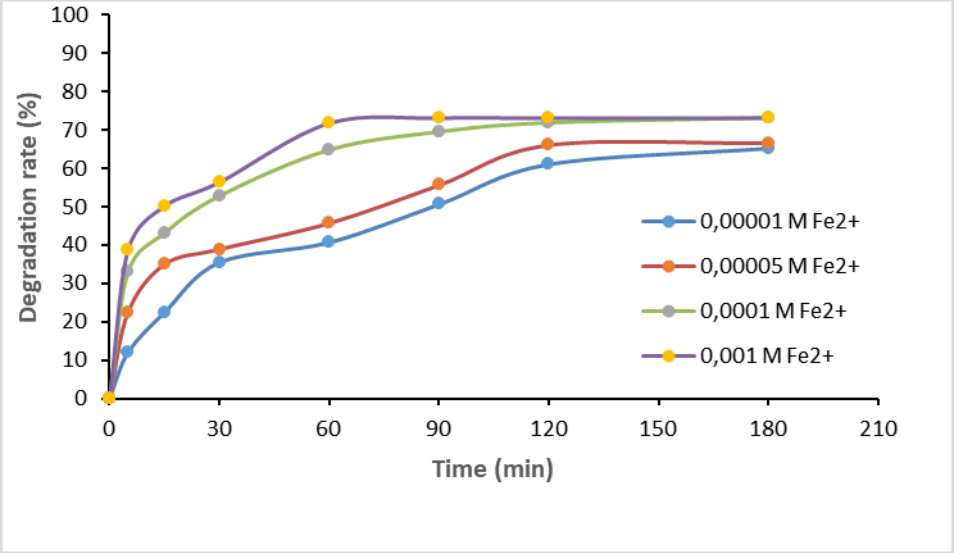

Figure IV. 8: The effect of Fe^{2+} ion concentration on BET removal

Experimental conditions : [BET] = 50 ppm; [H_2O_2] = 5×10^{-2} M; pH = 3; ƛ(max) = 530; t = 180 min.

Analysis of the curve reveals a gradual improvement in the dye degradation rate as the Fe^{2+} ion concentration increases, reaching maximum efficiency at 0.001 M. This optimal performance is linked to the increased generation of hydroxyl radicals (•OH) via the Fenton reaction, which promotes the degradation of the pollutant. However, beyond a certain threshold, an excess of Fe^{2+} can interfere negatively by consuming the free radicals through secondary reactions, thereby reducing their availability for dye oxidation. Furthermore, high concentrations can promote the formation of less reactive aqueous ferric complexes, reducing the overall efficiency of the process. These observations highlight the importance of determining an optimal catalyst concentration to maximize the yield of the degradation reaction.

IV.2.1.5 Effect of the initial concentration of the BET dye:

We conducted another series of experiments by varying the dye concentration within the range: 10 ppm; 50 ppm; 100 ppm, and 200 ppm. The pH was set to 3. The concentrations of hydrogen peroxide (H_2O_2) and ferrous ions were 5×10^{-2} M and 10^{-4} M, respectively.

The results of this series of experiments are presented in Figure IV.8

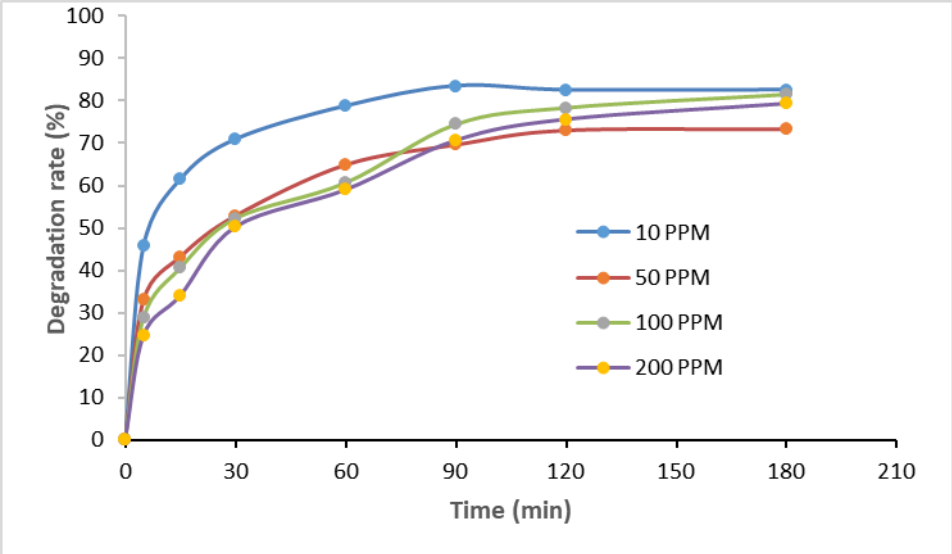

Figure IV. 9 : Effect of initial concentration C0 on the degradation of BET dye

Experimental conditions : $[Fe^{+2}] = 10^{-4}$ M; $[H_2O_2] = 5 \times 10^{-2}$ M; [pH] = 3; ƛ max = 530; t = 180 min.

The experimental results indicate that as the initial dye concentration increases, the degradation rate decreases. At low concentrations (10 ppm), the reaction is highly efficient, achieving a decolorization rate exceeding 80%. In contrast, at 200 ppm, this efficiency drops significantly. This decrease is explained by the fact that the hydroxyl radicals produced become insufficient to treat all the dye molecules present in the solution.

IV.2.2 The Effect of Agitation on the Degradation of the BET Dye:

Several tests were conducted by varying this parameter. To ensure comparable conditions, the other variables were kept constant: the dye concentration was set at 50 ppm, the pH was adjusted to 3, and the concentrations of H_2O_2 and Fe^{2+} were set at 5.10^{-2} M and 10^{-4} M, respectively.

The results obtained for the different stirring speeds tested are presented in Figure IV.9.

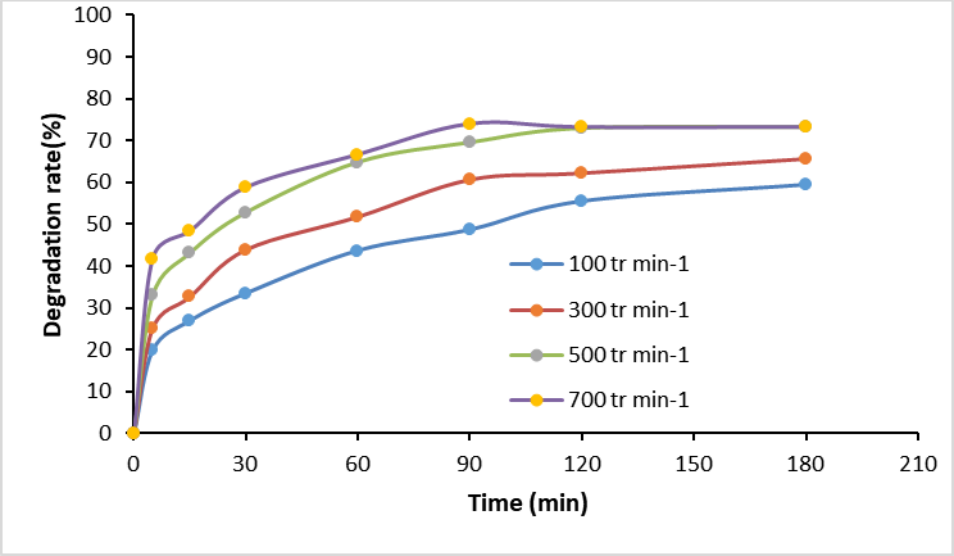

Figure IV. 10 : Effect of agitation on BET bleaching via the Fenton reaction

Experience requirement: [BET] = 50 ppm ; $[H_2O_2] = 5.10^{-2}M$; $[FeSO_4.7H_2O] = 10^{-4}M$;pH=3 ; λ_{max} = 530 nm ; t = 180 min.

To investigate the effect of stirring speed on dye degradation, The results shown in Figure IV.9 indicate that the rate of dye degradation increases with stirring speed. A gradual increase is observed as the speed increases from 100 to 700 rpm, with the maximum rate reached at 700 rpm. This trend can be explained by the fact that more intense stirring promotes homogeneous mixing of the reagents, thereby improving contact between the dye, hydrogen peroxide, and Fe^{2+} ions. This optimizes the generation of hydroxyl radicals •OH, the primary agents responsible for oxidation.

The speed of 700 rpm thus ensures effective dispersion of reactive species and better disruption of concentration gradients in the solution. At lower speeds (500, 300, and 100 rpm), turbulence is reduced, which can limit mass transfer and slow down the degradation kinetics.

IV.2.3 Effect of temperature on BET degradation :

The effect of temperature was confirmed by tests conducted at temperatures ranging from 25°C to 60°C. In these experiments, the dye concentration was set at 50 ppm at pH = 3, and the concentrations of hydrogen peroxide and ferrous ions were set at 5.10^{-2} M and 10^{-4} M, respectively.

The results of the experiments are shown in Figure IV.10

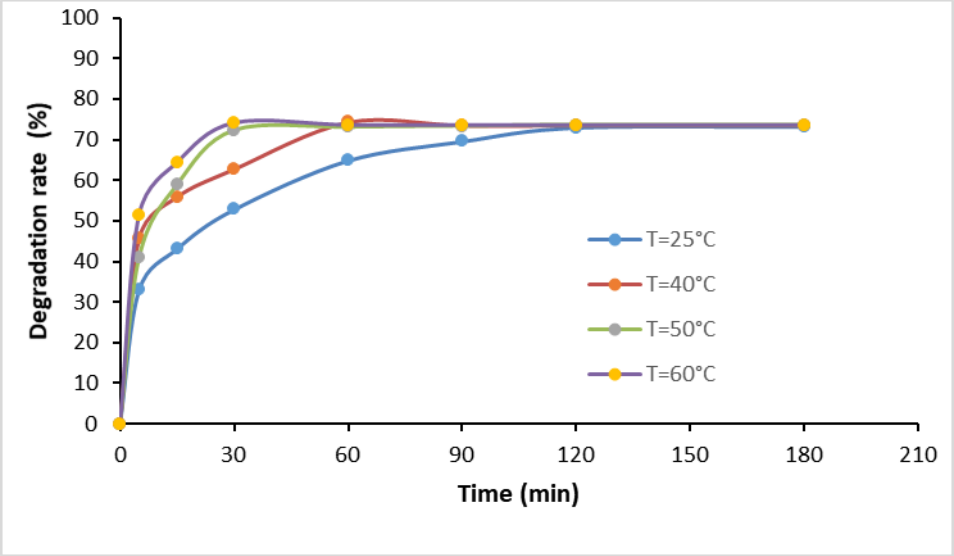

Figure IV. 11 : Effect of temperature on the decolorization of BET via the Fenton reaction.

Experience requirement: [BET] = 50 ppm ; $[H_2O_2] = 5.10^{-2}$M ; $[FeSO_4.7H_2O] = 10^{-4}$M ; pH=3 ; λ_{max} = 530 nm ; t = 180 min.

The study of the effect of temperature on degradation reveals a clear distinction between two patterns of behavior. At temperatures of 25°C and 40°C, degradation remains low and stable after 90 minutes, suggesting that the process is slow at low temperatures, likely due to insufficient thermal activation. In contrast, at 50°C and 60°C, degradation is significantly higher and reaches a similar plateau in both cases, indicating that temperature strongly promotes the reaction up to an optimal thermal threshold. Above 50°C, further increases in temperature no longer have a significant effect, suggesting that the system reaches saturation or that another factor becomes limiting. These results confirm that temperature plays a key role in activating the degradation process, up to a certain threshold beyond which the reaction no longer accelerates.

IV.3 Study of the influence of experimental parameters on the degradation of BET via the solar photo-Fenton process:

IV.3.1 Direct photolysis of the BET dye

A preliminary study was conducted to assess the potential degradation of BET under solar irradiation in the absence of the Fenton reagent. To this end, a solution of the dye at a concentration of 50 ppm was exposed to solar irradiation. The results obtained (Figure IV.11) indicate that the solution does discolor, but very slowly. It took 3 hours of irradiation to observe a decrease of

approximately 2% in the initial concentration of BET. These data confirm that the degradation of the dye by direct photolysis is very limited.

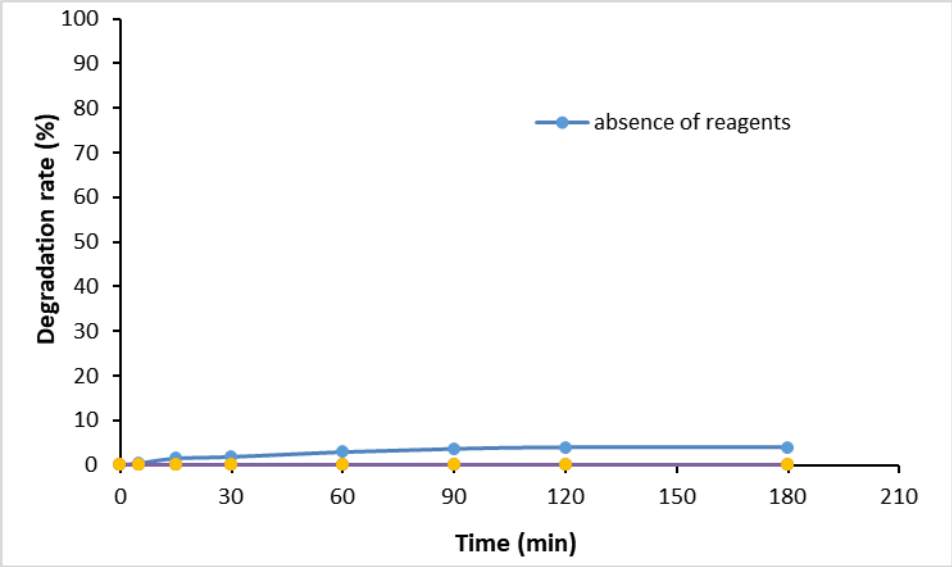

Figure IV. 12: Direct photolysis of BET dye at a concentration of 50 ppm.

IV.3.2 Study of the influence of certain experimental parameters on the degradation of BET via the photo-Fenton process

IV.3.2.1 Effect of pH

The effect of pH on the rate of black eriochrome t oxidation via the photo-Fenton process was studied over a pH range of 1 to 5.9. The initial operating conditions were as follows: the concentrations of BET, Fe(II), and H_2O_2 were 50 ppm, 10^{-4} M, and 5×10^{-2} M, respectively. The results, showing the evolution of the degradation rate as a function of pH, are presented in Figure IV.12.

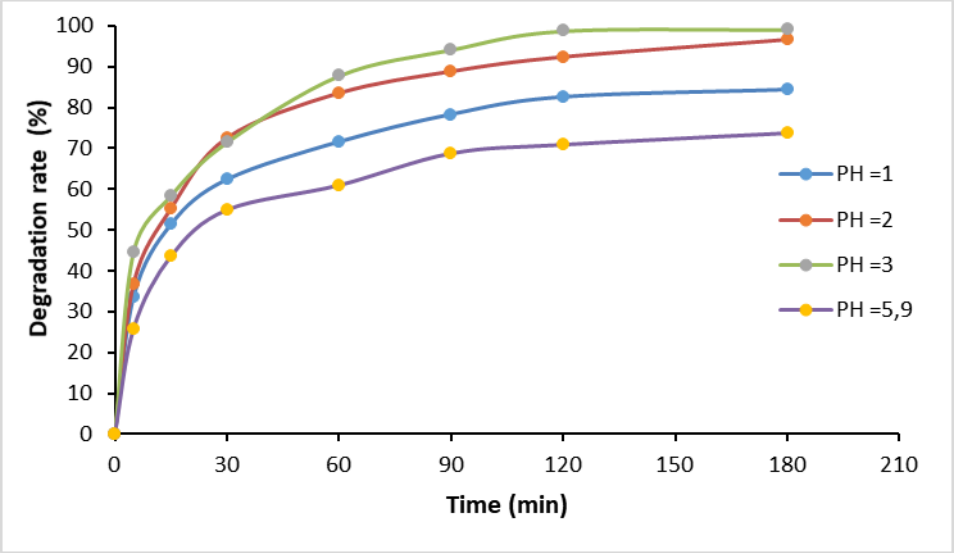

Figure IV. 13: Effect of pH on the discoloration of BET following exposure to sunlight

Experimental conditions: [BET] = 50 ppm, $[H_2O_2] = 5.10^{-2}$ M, $[Fe^{2+}] = 10^{-4}$ M, λ(max) = 530 nm

According to the results presented in Figure III.9, the efficiency of eriochrome black t degradation increases gradually as the pH rises from 1 to 3. However, a decrease in this efficiency is observed when the pH exceeds 3, particularly between 3 and 5.9. Thus, a pH of 3 can be considered optimal for the photo-Fenton process. This result is consistent with those reported in the literature, where an optimal pH of approximately 2.9 has been mentioned [67]. The decrease in efficiency at higher pH values is attributed to the precipitation of ferric ions as $Fe(OH)_3$, a highly stable compound. This precipitation limits the reduction of Fe^{3+} to Fe^{2+}, which slows down the regeneration of Fe^{2+} essential for the formation of hydroxyl radicals (•OH) making this step the rate-limiting step in the overall mechanism.

For pH values below 3, BET degradation is primarily limited by the interaction between ferrous iron and hydrogen peroxide. Indeed, the latter becomes highly unstable due to the formation of the oxonium ion ($H_3O_2^+$) through proton solvation. This electrophilic form of hydrogen peroxide significantly reduces its reactivity with ferrous iron. Consequently, the production of hydroxyl radicals resulting from the decomposition of H_2O_2 by Fe^{2+} (Fenton reaction) decreases significantly, thereby slowing the degradation of the BET. Based on these results, a pH of 3 is selected as the optimal value for further studies.

IV.3.2.2 Effect of hydrogen peroxide concentration

The concentration of hydrogen peroxide is a key parameter in the photo-Fenton process. With this in mind, we sought to identify the optimal concentration of H_2O_2 to improve treatment efficiency. By keeping the concentration of ferrous ions constant at 10^{-4} M and setting the pH of the medium to 3, we varied the H_2O_2 concentration from 10^{-3} to 10^{-1} M. Figure IV 13 illustrates the evolution of the decolorization rate of (BET) as a function of irradiation time for the different hydrogen peroxide concentrations tested.

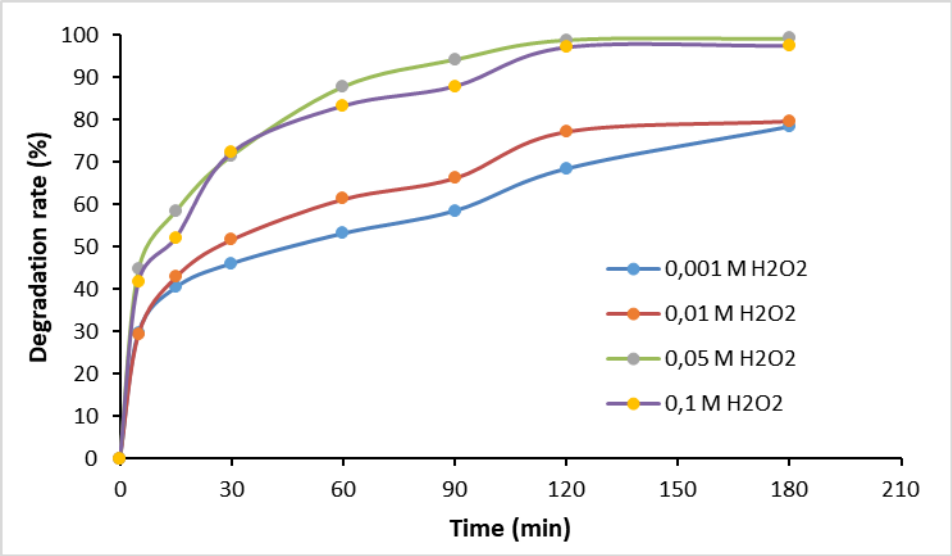

Figure IV. 14: Effect of H_2O_2 concentration on the decolorization of BET using the solar photo-Fenton process.

Experimental conditions: [BET] = 80 ppm; [$FeSO_4 \cdot 7H_2O$] = 10^{-4} M; pH = 3; λ_(max) = 530 nm; t = 180 min; T = 19.2°C.

Analysis of Figure III.7 shows that increasing the hydrogen peroxide concentration from 10^{-3} to 5×10^{-2} M improves the efficiency of the photo-Fenton process. In contrast, a higher concentration, such as 0.1 M, results in a slight decrease in degradation performance of eriochrome black t. Thus, the optimal concentration of H_2O_2 can be estimated at 5×10^{-2} M. This initial improvement is due to the increased production of hydroxyl radicals (•OH), which are essential for the oxidation of organic compounds. However, at concentrations that are too high, H_2O_2 can interfere with the process by consuming the hydroxyl radicals via side reactions, as illustrated by reaction IV.4 [68] .

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet}$ (IV.4)

IV.3.2.3 Effect of Fe^{2+} concentration

To evaluate the effect of ferrous ion (Fe^{2+}) concentration on the removal of eriochrome black t (BET) via the photo-Fenton process, experiments were conducted while maintaining the optimal hydrogen peroxide concentration at 5×10^{-2} M, as previously determined. The Fe^{2+} concentration was gradually increased from 10^{-5} to 10^{-3} M, while the pH of the reaction medium was fixed at 3. The results of this study are illustrated in Figure IV.14.

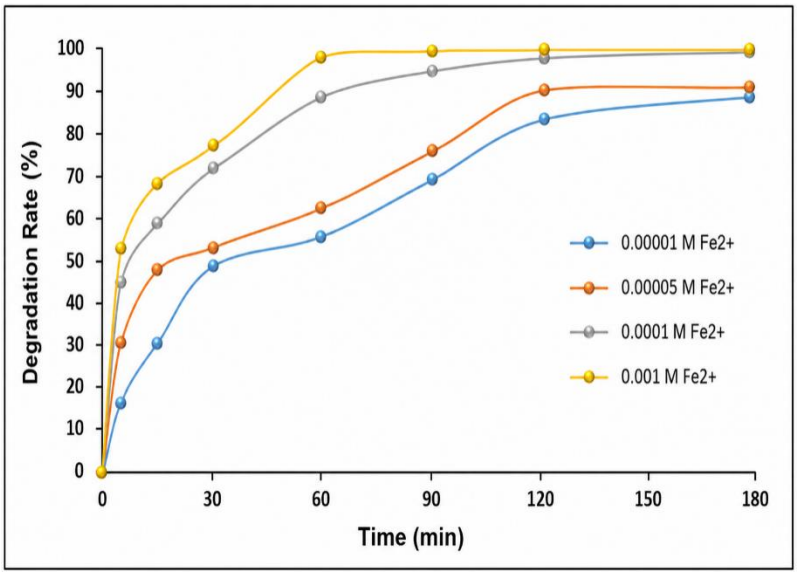

Figure IV. 15: Effect of $FeSO_4 \cdot 7H_2O$ concentration on the decolorization of BET using the solar photo-Fenton process.

Experimental conditions: [BET] = 50 ppm; $[H_2O_2] = 5.10^{-2}$ M; pH = 3; λ_(max) = 530 nm; t = 180 min; T = 19.2°C.

Figure IV.14 shows that increasing the Fe^{2+} ion concentration from 10^{-5} to 10^{-4} M significantly accelerates the decolorization of (BET). In contrast, a higher concentration, up to 10^{-3} M, results in a slight decrease in the rate of decolorization. Thus, a concentration of 10^{-4} M is selected as the optimal value for ferrous ions for the remainder of the study.

The effect of Fe^{2+} concentration can be interpreted in two stages: first, an increase in this

concentration promotes the production of hydroxyl radicals •OH, resulting from Fenton reactions (IV.1) and photoreduction (IV.2):[75].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad (IV.1)$$

$$[Fe(OH)]^{2+} + hv \rightarrow Fe^{2+} + \bullet OH \qquad (IV.2)$$

Next, an excess of Fe^{2+} (10^{-3} M) triggers a competitive reaction (IV.2) that consumes hydroxyl radicals, resulting in a decrease in the degradation yield:

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \qquad (IV.3)$$

IV.3.2.4 Effect of the concentration of Eriochrome Black T

The efficiency of the photo-Fenton process can be affected by the amount of pollutant present in the solution. Therefore, we sought to investigate the effect of BET concentration on degradation via this process. The concentrations examined were: [BET] = 10, 50, 100 and 200 ppm; the results are shown in Figure IV.15

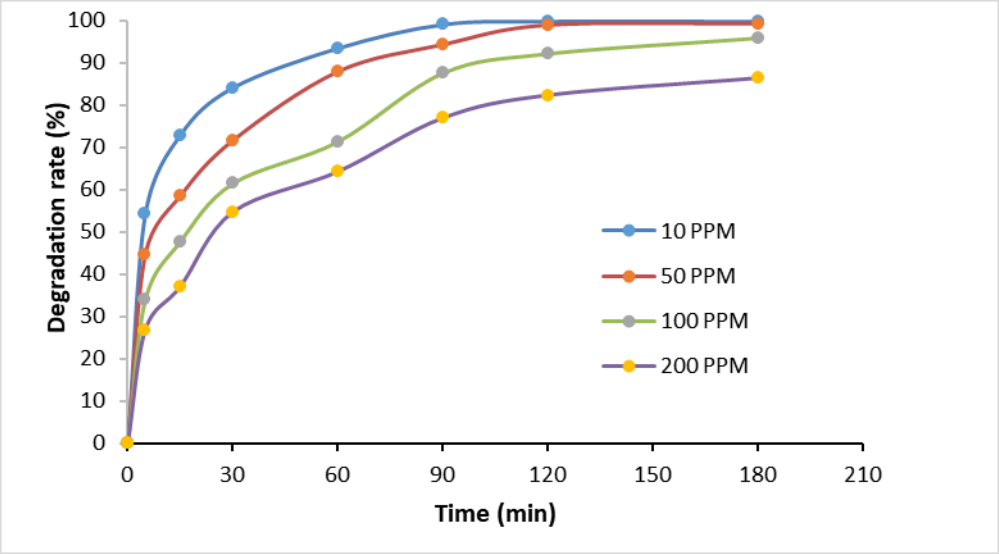

Figure IV. 16: Effect of the initial concentration C0 on the degradation of BET dye by the solar photo-Fenton process.

Experimental conditions: [H_2O_2] = 5.10^{-2} M; [$FeSO_4 \cdot 7H_2O$] = 10^{-4} M; pH = 3; λ_(max) = 530 nm; t = 180 min; T = 18.9°C.

Analysis of the figure above reveals that an increase in the initial dye concentration leads to a gradual decrease in its degradation rate under solar irradiation. At a concentration of 10 ppm, degradation is rapid and reaches nearly 100% in less than 60 minutes. At a concentration of 50

ppm, the process remains effective, although the rate of degradation is slightly reduced. In contrast, at concentrations of 100 ppm and above, a noticeable slowdown in the degradation kinetics is observed, while at 200 ppm, residual coloration remains visible even after 180 minutes of treatment. This decrease in photocatalytic efficiency can be attributed to the screening effect created by the high dye concentration, which limits the penetration of solar radiation into the reaction medium and reduces the activation of the photocatalyst. Consequently, the production of reactive species responsible for dye oxidation decreases, slowing the overall degradation of the pollutant.

IV.3.3 The effect of agitation on the degradation of BET dye:

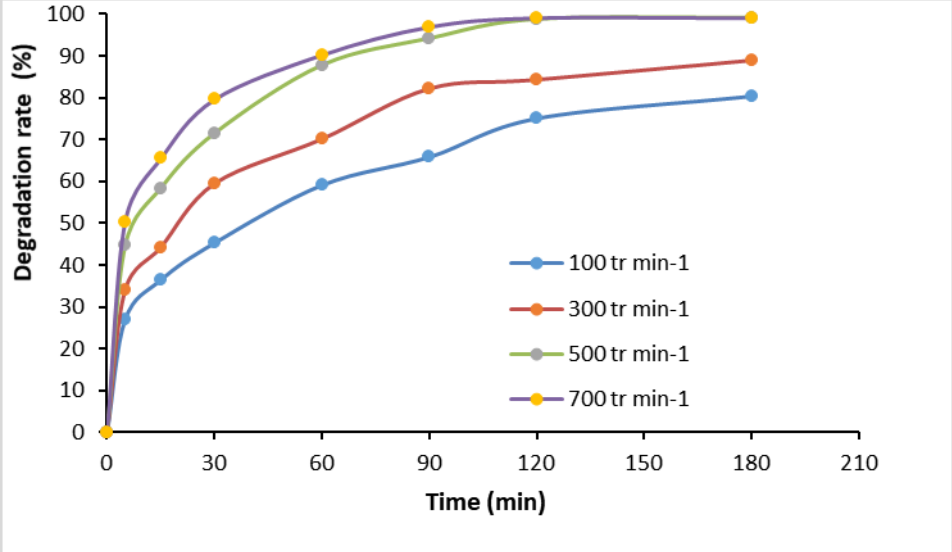

Figure IV. 17: Effect of agitation on the decolorization of BET via the Fenton

Experimental conditions: [BET] = 50 ppm; [H_2O_2] = 5.10^{-2} M; [$FeSO_4 \cdot 7H_2O$] = 10^{-4} M; pH = 3; λ_(max) = 530 nm; t = 180 min; T = 12.3°C.

Analysis of the graph highlights the influence of stirring speed on the efficiency of dye degradation. The results show that an increase in stirring speed leads to a gradual improvement in the degradation rate. At a speed of 700 rpm, degradation reaches nearly 100% after 120 minutes of treatment, whereas at 100 rpm, it remains below 80% even after 180 minutes. This improvement can be attributed to better homogenization of the reaction medium, promoting contact between the dye molecules and the active sites of the photocatalyst, as well as to a reduction in mass transfer limitations. However, the difference observed between 500 and 700 rpm remains relatively small,

suggesting that the optimal stirring speed is close to this range and that a further increase yields only a limited gain in degradation efficiency.

IV.3.4 Effect of temperature on BET degradation:

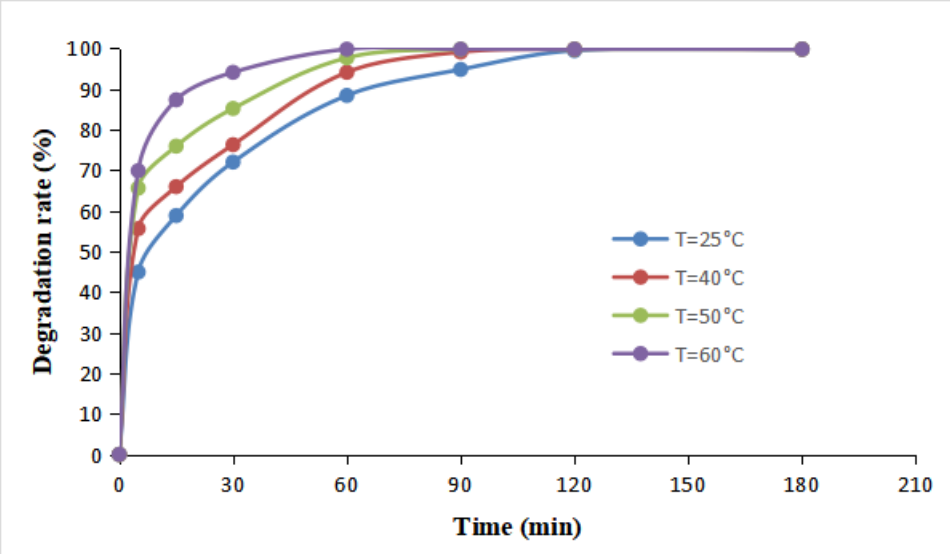

Figure IV. 18: Effect of temperature on the decolorization of BET using the solar Photo-Fenton process.

Experimental conditions: [BET] = 50 ppm; [H_2O_2] = 5 × 10^(−2) M; [$FeSO_4 \cdot 7H_2O$] = 10^{-4} M; pH = 3; λ_(max) = 530 nm; t = 180 min.

Analysis of the graph highlights the positive influence of temperature on the degradation of BET via the photo-Fenton process under solar irradiation. The results show that an increase in temperature leads to a significant improvement in the degradation rate. At 25 °C, degradation reaches approximately 85% after 180 minutes of treatment, whereas at 60 °C, it reaches nearly 100% in less than 60 minutes. This improvement is attributed to the acceleration of oxidation reactions induced by the rise in temperature, which promotes interactions between reactive species and pollutant molecules. Furthermore, the increase in temperature stimulates the production of hydroxyl radicals (•OH), the primary oxidizing agents in the photo-Fenton process, which enhances degradation efficiency and reduces the time required to eliminate the pollutant.

IV.3.5 Comparison of the Fenton and solar photo-Fenton processes

Figure IV.17 compares the performance of the Fenton and solar photo-Fenton processes in the degradation of BET. The results clearly show that, throughout the treatment period, the solar

photo-Fenton process exhibits greater efficiency than the conventional Fenton process. After 2 hours of treatment, the degradation rates of BET reached 56% for the Fenton process and 96% for the solar photo-Fenton process, respectively.

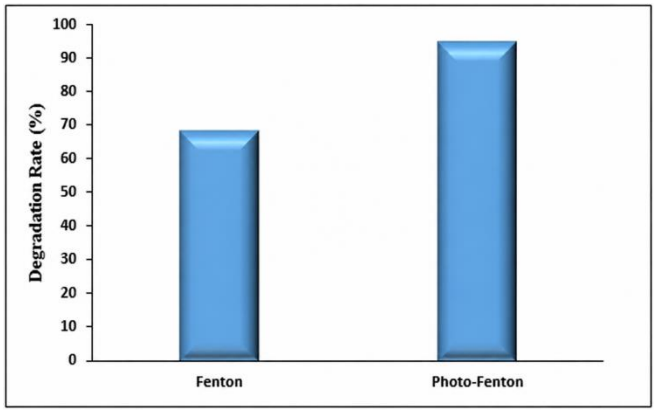

Figure IV. 19: Time-dependent degradation rates during the treatment of BET using the Fenton and solar photo-Fenton processes.

This significant difference highlights the beneficial effect of solar radiation, which promotes the regeneration of ferrous ions (Fe^{2+}) from ferric ions (Fe^{3+}) and stimulates the production of hydroxyl radicals (•OH), the primary agents responsible for the oxidation of the pollutant. However, this difference in efficiency cannot be attributed solely to the direct photolysis of the pollutant, whose contribution remains low. The observed improvement results primarily from the synergy between the Fenton reaction and the photochemical reactions induced by solar radiation, enabling continuous and increased generation of hydroxyl radicals. Thus, unlike the conventional Fenton process, where •OH radicals are produced primarily by the reaction between Fe^{2+} and H_2O_2, the solar photo-Fenton process also benefits from the photoreduction of hydroxylated ferric complexes and the photolysis of hydrogen peroxide, which considerably increases the degradation efficiency of BET.

Table IV. 1 : Production of •OH radicals via the Fenton and solar photo-Fenton processes

Treatment process	Chemical reaction	Pathway for the formation of •OH radicals
Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- +$ •OH ()	Fenton reaction
Solar Photo-Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- +$ •OH ()	Photo-Fenton reaction
	$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} +$ •OH ()	Photolysis of Fe(III) complexes under sunlight
	$H_2O_2 + h\nu \rightarrow 2$•OH ()	Photolysis of hydrogen peroxide under sunlight

This comparison confirms that combining the Fenton process with solar irradiation accelerates the production of oxidizing species and results in a much faster and more complete degradation of BET.

General Conclusion

General Conclusion

The main objective of this work was to compare the performance of two advanced oxidation processes, namely the Fenton and solar photo-Fenton processes, for the treatment of water contaminated with colored effluents, while optimizing the parameters influencing the degradation kinetics.

The experimental study focused on the degradation of Eriochrome Black T (BET) in an acidic aqueous medium. Eriochrome Black T is an azo dye used in various industrial and analytical applications, particularly as a complexometric indicator. The bibliographic study highlighted the characteristics of synthetic dyes, the conventional methods used for wastewater treatment, as well as the potential offered by advanced oxidation processes (AOPs).

The main findings of this study can be summarized as follows:

The Fenton process proved to be highly effective for the decolorization of EBT at an optimal pH value of 3.

The treatment efficiency strongly depends on the concentrations of the oxidizing agent (H_2O_2) and the catalyst (Fe^{2+}). The optimal concentrations were determined to be 5×10^{-2} mol·L^{-1} for hydrogen peroxide and 10^{-4} mol·L^{-1} for ferrous ions. Beyond these values, a decrease in efficiency was observed due to side reactions leading to the non-productive consumption of hydroxyl radicals.

The degradation rate increased as the initial dye concentration decreased. Thus, for concentrations below 10 ppm, decolorization occurred more rapidly, whereas higher dye concentrations significantly slowed down the process.

An increase in temperature enhanced the reaction kinetics and reduced the time required for dye decolorization.

The solar photo-Fenton process (Fe^{2+}/H_2O_2/solar radiation) exhibited higher efficiency than the conventional Fenton process. Under the same operating conditions, it achieved a decolorization rate of 99% after 180 minutes of treatment.

In conclusion, the results confirm the effectiveness of advanced oxidation processes for the treatment of water contaminated with refractory organic compounds. Among the investigated methods, the solar photo-Fenton process proved to be the most efficient due to the synergistic effect of solar radiation, which promotes the regeneration of Fe^{2+} ions and the continuous production of hydroxyl radicals. Therefore, this technology represents a promising, efficient, and

environmentally friendly solution for the treatment of industrial wastewater.

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RESUME

Cette étude compare l'efficacité des procédés Fenton et photo-Fenton solaire pour l'élimination du colorant Noir Eriochrome T (NET) dans les mêmes conditions opératoires.

Les résultats montrent que les conditions optimales sont pH = 3, $H_2O_2 = 5\times10^{-2}$ mol·L^{-1} et $Fe^{2+} = 10^{-4}$ mol·L^{-1}.Une faible concentration initiale du colorant (<10 ppm) améliore la cinétique de dégradation, tandis qu'une concentration élevée la ralentit.Le procédé photo-Fenton solaire est plus performant, atteignant environ 99 % de décoloration en 180 minutes.

Mots-clés : NET, procédé Fenton, photo-Fenton solaire, oxydation avancée, traitement des eaux.

ABSTRACT

This study compares the efficiency of Fenton and solar photo-Fenton processes for the removal of Eriochrome Black T (BT) under identical operating conditions.The optimal conditions are pH = 3, $H_2O_2 = 5\times10^{-2}$ mol·L^{-1}, and $Fe^{2+} = 10^{-4}$ mol·L^{-1}.Lower initial dye concentration (<10 ppm) enhances degradation, while higher concentrations slow the reaction.

The solar photo-Fenton process shows higher efficiency, achieving about 99% decolorization within 180 minutes.

Keywords: BET, Fenton process, solar photo-Fenton, advanced oxidation processes, wastewater treatment

ملخص

تهدف هذه الدراسة إلى مقارنة فعالية عمليتي فنتون والفوتو-فنتون الشمسي في إزالة صبغة Eriochrome Black T (BET) من المياه الملوثة تحت نفس الظروف التشغيلية.أظهرت النتائج أن الظروف المثلى لكلا العمليتين هي pH = 3، مع تركيز $H_2O_2 = 5\times10^{-2}$ مول/لتر و$Fe^{2+} = 10^{-4}$ مول/لتر.كما أن انخفاض تركيز الصبغة (<10 ملغ/ل) يحسن سرعة التحلل، بينما يبطئ ارتفاع التركيز التفاعل.وقد حقق الفوتو-فنتون الشمسي كفاءة أعلى، حيث وصلت نسبة الإزالة إلى حوالي 99% خلال 180 دقيقة.

الكلمات المفتاحية : (BET ،Eriochrome Black T ،فنتون، الفوتو-فنتون الشمسي، الأكسدة المتقدمة، معالجة المياه.