



# Treball Final de Grau

**Research study of the operational parameters affecting the different Fenton processes to reduce the presence of dyes in textile effluents**

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## SUMMARY

Water pollution is an environmental problem that has increased over the years, due to an increase in water consumption by the population and industry. The textile industry is the second most water-consuming manufacturing, and therefore generates a considerable amount of wastewater, which needs to be accurately treated for the re-use. These wastewaters are characterised by having highly toxic organic compounds and colouring agents, which are part of the group of emerging pollutants (EPs).

Emerging pollutants (EPs) are compounds present in the environment that have high toxicity and persistence. Besides, these compounds begin to be regulated by law, and there are concerns about the possible consequences they may cause. The elimination of most of these emerging contaminants cannot be carried out by conventional treatments due mainly to their low biodegradability and high stability.

Advanced oxidation processes (AOPs) are alternative treatments capable of eliminating these poorly biodegradable compounds. These techniques, based on the generation of high oxidizing power species such as hydroxyl radicals ( $\cdot\text{OH}$ ), can oxidize chemical compounds and completely mineralize the organic contaminants present in wastewater. The different Fenton processes are also part of the group of advanced oxidation processes and are very promising technologies for the treatment of textile effluents.

The purpose of this work is to investigate the different operational parameters that affect the efficiency of Fenton processes, for the abatement of two representative dyes, indigo carmine and methyl orange. It is performed a bibliographical revision of several scientific papers, which focus on explaining and studying some of the factors that influence on the degradation process of these dyes. The following techniques have been considered: classical Fenton, Photo-Fenton, Photo-Fenton-Like, Electro-Fenton and Photo-Electro-Fenton. The use of a lower dye concentration, a Boron-Doped Diamond (BDD) anode in the Electro-Fenton process, the

incorporation of ultraviolet radiation or the need to acidify the solution, up to a pH value around 3, are some essential factors that allow better abatement of the dyes, according to the consulted literature.

Besides, this document also shows an experimental part, in which is performed the discolouration of an indigo carmine solution through the Photo-Fenton process at circumneutral pH, using Diethylenetriaminepentaacetic acid (DTPA) as the chelating agent to avoid iron precipitates, thus making the process more applicable on an industrial scale. The process to evaluate occurs in a reactor using different artificial light sources (*black light blue*, BLB and *light-emitting diode*, LED), with different BLB lamp powers (8 W and 24 W) and with different initial concentrations of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 200 ppm and 100 ppm).

The best results from the experimental part are obtained using BLB lamps with a 24 W power and an initial oxidant concentration of 200 ppm. A 98.1% of discolouration was achieved in 100 minutes of reaction, using concentrations of 50 ppm of indigo carmine dye and 5 ppm of  $\text{Fe}^{2+}$ . Besides, the application of DTPA as a chelating agent has allowed the catalyst ( $\text{Fe}^{2+}$ ) to remain soluble.

**Keywords:** Fenton, Photo-Fenton, Photo-Fenton-Like, Electro-Fenton, Photo-Electro-Fenton, pH circumneutral, chelating agent, indigo carmine, methyl orange, advanced oxidation processes, emerging pollutants, discolouration, abatement, light source.

## RESUM

La contaminació de l'aigua és un problema mediambiental que s'ha vist incrementat al llarg dels anys, degut a un augment en el consum d'aigua per part de la població i de la indústria. La indústria tèxtil és la segona indústria que més aigua consumeix, i per tant, genera una gran quantitat d'aigües residuals, que necessiten ser tractades correctament per la seva reutilització. Aquestes aigües residuals es caracteritzen per contenir compostos orgànics altament tòxics i agents colorants, que formen part del grup de contaminants emergents (CEs).

Els contaminants emergents són compostos que existeixen al medi ambient i, que presenten una elevada toxicitat i persistència. A més, aquests compostos comencen a estar regulats per la llei, i preocupa les possibles conseqüències que puguin provocar. L'eliminació de la majoria d'aquests contaminants emergents no es pot realitzar mitjançant els tractaments convencionals degut principalment a la seva baixa biodegradabilitat i elevada estabilitat.

Els processos d'oxidació avançada (POAs) són uns tractaments alternatius capaços d'eliminar completament aquests compostos poc biodegradables. Aquestes tècniques es basen en la generació d'espècies amb un elevat poder oxidant, com els radicals hidroxil ( $\cdot\text{OH}$ ), els qual són capaços de oxidar complexos químics i mineralitzar completament els contaminants orgànics presents a les aigües residuals. Els diferents processos Fenton formen part també del grup dels processos d'oxidació avançada, i són tecnologies prometedores pel tractament dels efluent tèxtils.

El propòsit d'aquest treball és investigar els diferents paràmetres operacionals que afecten a l'eficiència dels processos Fenton per la reducció de dos colorants representatius, l'indi de carmí i el taronja de metil. Es duu a terme una revisió bibliogràfica de diferents articles científics, que estudien els diversos factors que influeixen en el procés de degradació d'aquests colorants. S'han considerat les següents tècniques: Fenton clàssic, Foto-Fenton, Foto-Fenton-Like, Electro-Fenton i Foto-Electro-Fenton. L'ús d'una concentració de colorant més baixa, d'un

ànode de BDD en el procés Electro-Fenton, la incorporació d'una radiació ultraviolada o la necessitat d'acidificar la solució, fins a un valor de pH al voltant de 3, són alguns d'aquests factors claus que permeten obtenir una millor reducció del colorant, segons la bibliografia consultada.

A més, també es mostra una part experimental on es duu a terme la decoloració d'una solució d'indi de carmí per mitjà del procés Foto-Fenton a un pH circumneutral, utilitzant el DTPA com agent quelant per evitar la precipitació del ferro, fent així que el procés sigui més aplicable a escala industrial. La reacció es produeix a un reactor utilitzant diferents fonts llumíniques artificials (*black light blue*, BLB i *light-emitting diode*, LED), amb diferents potències de les làmpades BLB (8 W i 24 W) i amb diferents concentracions inicials de peròxid d'hidrogen ( $\text{H}_2\text{O}_2$ , 200 ppm i 100 ppm).

Els millors resultats de la part experimental s'han obtingut utilitzant les làmpades BLB amb una potència de 24 W i una concentració inicial d'oxidant de 200 ppm. Es va aconseguir una decoloració del 98.1% en 100 minuts de reacció, utilitzant 50 ppm de indi de carmí i 5 ppm de  $\text{Fe}^{2+}$ . A més, l'ús del DTPA com agent quelant ha permès que el catalitzador ( $\text{Fe}^{2+}$ ) es mantingui soluble.

**Paraules clau:** Fenton, Foto-Fenton, Foto-Fenton-Like, Electro-Fenton, Foto-Electro-Fenton, pH circumneutral, agent quelant, indi carmí, taronja de metil, processos d'oxidació avançada, contaminants emergents, decoloració, reducció, font llumínica.

# 1. INTRODUCTION

## 1.1. WATER RESOURCES

The total amount of water available on planet Earth is approximately 1386 million km<sup>3</sup> [1] [2]. Some 97.5% of this total water on Earth's surface is classified as salt water, while the remaining 2.5% can be classified as freshwater. Of the total freshwater stock, approximately less than 1% is available only to humans and to the ecosystem [1] [2].

About the use of this available water, roughly 70% corresponds to that used in agriculture, 19% is used in the industrial sector, including energy, and only 11% is used in the domestic arena. Besides, water demand is expected to increase further in the future due to the increasing need for water, mainly from industry and agriculture, but also by domestic use [3]. The real problem which needs to be solved to have this availability of water is the current water pollution.

## 1.2. WASTEWATER FROM THE TEXTILE INDUSTRY

As mentioned recently, the industry is one of the most water-intensive sectors. Within this sector, the textile industry is the second-largest industrial consumer of water in the world, according to a UN study published in April 2018 [4]. This means that it is also considered one of the industries that generate more wastewater. These wastewaters of textile origin are generated during the different stages that make up the textile manufacturing process, but above all, the dyeing and finishing treatments produce around 17 – 20% of these industrial effluents [5].

### 1.2.1. Features of wastewater from the textile industry

Wastewater from the textile industry is characterized by a significant amount of highly polluting organic chemicals and colouring agents, mostly soluble and with low biodegradability

[6]. Others aspects that define these textile effluents, coming mainly from the dyeing and finishing processes, are the low content of colloidal and suspended matter, the high variability of flow and pollution load, a Chemical Oxygen Demand (COD) approximately twice that of an urban effluent and, principally high colouring and salinity [7].

Textile industries have to control different polluting parameters in their wastewaters to fulfil the regulations established by the authorities. The Biochemical Oxygen Demand (BOD), COD and Total Organic Carbon (TOC) are the parameters used for quantifying organics pollutions, in textile effluents. Nitrogen and phosphorous indicate the presence of nutrients, conductivity shows the presence of salts, and inhibitory matter measures the toxicity degree. Besides, suspended matter and colour are other parameters that must also be controlled [7].

### 1.3. EMERGING POLLUTANTS

In recent years, the development of new methods of analysis has made it possible to discover the presence of other potentially dangerous contaminants, known as emerging pollutants [10]. These emerging pollutants are defined as chemicals present in the environment at low concentrations, that begin to be generally controlled and that have a detrimental effect on both human health and environmental ecosystems [11].

Several groups of compounds can be classified as emerging pollutants. Among them, the drugs of abuse, pharmaceuticals, personal hygiene products, steroids and hormones, petrol additives and their processing products, surfactants or additives, and industrial agents encompass the main types of emerging pollutants [12].

#### 1.3.1. Dyes

Dyes are substances that also form part of the emerging contaminants group. Around  $7 \times 10^7$  tonnes of synthetic dyes are produced annually for textile industries worldwide. Approximately 10% of this total is discharged into the environment as waste from the textile industry after dyeing and processing [13]. The presence of dyes in textile effluents, even at very low concentrations, could be highly visible and undesirable [14]. It is important to concern about the fact of textile effluents colour and, above all, the fact that many of these dyes are toxic and





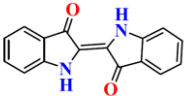
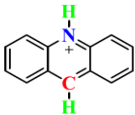
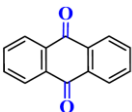
mutagenic to health. Without adequate treatment, many dyes are stable and may remain in the environment for a long time [15].

Dyes are characterized by being organic compounds that have the capacity of absorbing radiation from light in the visible spectrum, more accurately from 380 to 750 nm. The transformation of white light into coloured light, by reflection on a body or by diffusion, is due to the selective absorption of certain groups of atoms, known as chromophores. Dyes have three essential groups in their molecules: the chromophore group, the auxochrome group and the matrix [13].

The chromophore group is responsible for the colour formation since it allows absorbing electromagnetic radiation of different wavelengths due to the exciting electron of the molecule [13] [16].

Dyes can be classified mainly according to the colour, the source, the colour index (C.I.), ionization type, the molecular structure or the type of chromophore group [16] [17]. Table 1 shows the classification of different kinds of dyes according to their chromophore group [13].

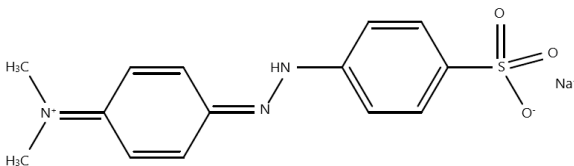
**Table 1.** Classification of some textile dyes based on the chromophore group. (Table adapted from [13]).

| CLASS        | CROMOPHORE  | EXAMPLE         |
|--------------|---|-----------------|
| Azo          |    | Methyl orange   |
| Nitro        |  | Picric acid     |
| Indigoid     |  | Indigo carmine  |
| Acridine     |  | Acridine orange |
| Antraquinone |  | Acid blue 40    |

### 1.3.1.1. Methyl orange

Methyl orange, also known as orange III or helianthin, is a dye with chemical formula  $C_{14}H_{14}N_3NaO_3S$  that belongs to the family of azo dyes, which are characterized by being an aromatic compound that have one or several azo bonds. Methyl orange (Figure 1) is an orange crystalline powder – yellowish and odourless. Also, this dye has a high melting point, higher than  $300\text{ }^{\circ}\text{C}$ , and is soluble in water but insoluble in alcohol [18] [19]. Methyl orange is one of the most commonly used tint dyes in the textile industry. It also can be employed as chemical indicators to analyse chemical and pharmaceutical substances [18].

The addition of dyes such as methyl orange to water has been shown to cause a huge impact on water quality, due to its toxicity, mutagenic and carcinogenic nature [20].

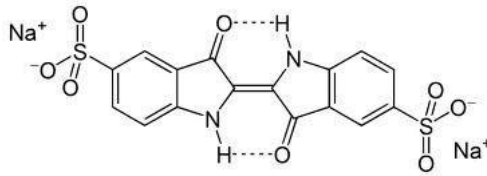


**Figure 1.** Chemical structure of methyl orange dye (MO).

### 1.3.1.2. Indigo carmine

Indigo carmine, also known as acid blue 74, is also one of the most commonly used dyes in the textile industry. This dye (Figure 2) with chemical formula  $C_{16}H_8N_2Na_2O_8S_2$  is a dark purple crystalline powder that belongs to the family of indigoid dyes. It has a high melting point, above  $300\text{ }^{\circ}\text{C}$ , and its solubility in water is  $1\text{g}/100\text{mL}$  [16] [21]. Its main application is in the textile industry, for blue jeans and other blue Denim products [16]. However, it is also used as an additive in pharmaceutical tablets and capsules or for medical purposes [22].

This dye is highly toxic and carcinogenic, as it can cause reproductive, developmental, neuronal and acute toxicity, as well as tumours at the site of application. It is also known to have different cardiovascular and respiratory effects and to cause possible hypertension [22].



**Figure 2.** Chemical structure of indigo carmine dye (IC). (Figure taken from [21]).

Methyl orange and indigo carmine, two dyes widely used mainly in the textile industry, are examples of organic synthetic pigments that produce a high environmental and human health risk, due to their high toxicity and the high carcinogenic risk of their products [23]. For this and more reasons, the elimination of these dyes, which are present in textile effluent, among others, is a need of the first order nowadays.

## 1.4. TREATMENTS OF TEXTILE INDUSTRY WASTEWATER

Textile effluents are subjected to different treatments, to ensure the removal or recovery of organic compounds to the required degree by the legislation that regulates the discharge of the fluid [24]. The effectiveness of the treatment varies according to the type and concentration of dyes, the concentration of other substances present in effluents and how the contaminated waters are shown. For these reasons, it is necessary to know an accurate composition of textile effluents to select the most appropriate type of treatment [25].

### 1.4.1. Conventional treatments

A wide variety of methods are available to treat wastewater from the textile industry polluted with dyes. Some of these treatments are very specific, with high costs, do not apply for a wide variety of colourants and do not solve the problem of discolouration [26]. These treatments can be classified into three main groups: physical treatments, chemical treatments and biological treatments. There is also the possibility to use a combination of these three different types of treatments.

### 1.4.1.1. Physical treatments

Physical treatments were the first methods used for wastewater's treatment. They are characterised by the predominance of the action of physical forces, by having a little environmental impact and by not achieving a complete degradation of pollutants [25]. These methods consist mostly of the transfer of pollutants from the liquid phase to the solid phase. Besides, further treatment is required to remove the residual sludge, thus increasing the total cost of the process [22]. Some examples of these physical methods are coagulation-flocculation, sedimentation, membrane filtration or adsorption [26] [27]. Table 2 shows the advantages and disadvantages of some physical methods [26] [27].

**Table 2.** Advantages and disadvantages of some physical methods for the treatment of textile effluents.

| Methods                  | Advantages  | Disadvantages  | References |
|--------------------------|---|--|------------|
| Adsorption               | It is an economically, attractive and efficient technology since it allows the removal of various dyes.         | Activated carbon has a high cost, and loss occurs in regeneration. Also, the least expensive materials require more contact time and generative waste. | 26         |
| Membrane filtration      | It allows the removal of dyes at low concentrations and is resistant to both temperature and microbial attacks. | It has a high cost, some are not completely efficient for the removal of dissolved solids, and therefore require additional treatments.                | 26         |
| Coagulation-flocculation | It allows for relatively rapid discolouration and a significant reduction in COD.                               | There is a sludge generation, it is a costly operation, coagulants are not reusable, and there is a specific colour reduction.                         | 27         |

### 1.4.1.2. Biological treatments

Biological treatment methods are based on the use of microorganisms to remove undesired components in wastewater, applying the metabolic activity of microorganism on these [24]. It consists of decreasing biodegradable organic matter, thus also reducing COD, BOD and toxicity [25].

Biological methods can be classified into bioabsorption, enzymatic methods and biodegradation. Depending on oxygen conditions, the latter can be classified as aerobic biodegradation or anaerobic biodegradation [26]. Table 3 shows the advantages and disadvantages of these three biological methods [26].

**Table 3.** Advantages and disadvantages of some biological methods for treatment of textile effluents (Table adapted from [26]).

| Methods        | Advantages   | Disadvantages  |
|----------------|--|--|
| Bioabsorption  | Microbial biomass is used for the absorption and removal of dyes from wastewater.        | Not used yet to treat large amounts of water because it is in the study stage.                 |
| Biodegradation | The use of mixed pools in combined aerobic/anaerobic systems allows the removal of dyes. | It requires a long phase of acclimatization and presents resistance to recalcitrant compounds. |
| Enzymatic      | It is very efficient for specific compounds and requires a short contact time.           | Enzymes are affected by a large number of parameters presents in wastewater.                   |

### 1.4.1.3. Chemical treatments

Chemical treatment methods are used basically for the elimination of hazardous organic compounds present in wastewater at low concentrations. They are sometimes applied as a pre-treatment of biological processes and thus reducing, among other things, the pollutant load [25].

Chemical oxidation and reduction, complexometric methods or ion exchange are some of the most commonly used chemical methods [27]. Table 4 shows the advantages and disadvantages of using some of these chemical methods.

**Table 4.** Advantages and disadvantages of various chemical methods for the treatment of textile effluents.

| Method             | Advantages  | Disadvantages  | Refer. |
|--------------------|---|--|--------|
| Chemical oxidation | It is one of the most commonly used methods, it involves the breaking of aromatic rings and different chemical oxidants can be used: O <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> -Fe <sup>2+</sup> or NaOCl. | The use of O <sub>3</sub> as a chemical oxidant is not very efficient for dispersed dyes. NaOCl generates toxic and carcinogenic sub-products. The use of H <sub>2</sub> O <sub>2</sub> -Fe <sup>2+</sup> produces sludge. | 26     |
| Chemical reduction | It is an effective method for the discolouration of azo dyes.   | There is the formation of aromatic amines, and their degradation is incomplete.  | 27     |
| Ion exchange       | There is regeneration, and the adsorbent is not lost.   | It is not useful for all types of dyes.  | 15, 16 |

The fact that textile effluents have different characteristics complicates the standardization in processes through traditional methods [4]. Moreover, the high stability and persistence of dyes in water also difficult their complete degradation by conventional techniques [25]. For these reasons, it has been developed new treatments able to completely discharge and mineralize the dyes or recalcitrant organic compounds present in the wastewater.

### 1.5. ADVANCED OXIDATION PROCESSES (AOP<sub>S</sub>)

Advanced oxidation processes (AOPs) are defined as processes that generate, normally at constant temperature and pressure, highly reactive radicals, such as hydroxyl radicals ( $\cdot\text{OH}$ ), in quantities adequate to oxidize the chemical compounds present in wastewater [28]. These

processes are effective alternatives to conventional treatment methods and allow the complete mineralization of organic contaminants present in textile effluents [29] [30]. Besides, they are considered relevant and useful for wastewater of textile origin because they manage to reduce the colour, toxicity, COD and odours thereof [31].

### 1.5.1. Mechanism of action

The common factor of all advanced oxidation processes is the use of hydroxyl radical ( $\cdot\text{OH}$ ) as oxidizing agent [22]. This hydroxyl radical is considered one of the most reactive oxidizing agents, with an oxidation potential of 2.8 V [30] [32]. Table 5 shows the oxidation potentials of different strong oxidants [32].

**Table 5.** Oxidation potential of some strong oxidizing agents (Table adapted from [32]).

| <b>Oxidizing agent</b> | <b>Oxidation potential [V]</b> |
|------------------------|--------------------------------|
| Fluorine               | 3.03                           |
| Hydroxyl radical       | 2.80                           |
| Atomic oxygen          | 2.42                           |
| Ozone                  | 2.07                           |
| Hydrogen peroxide      | 1.78                           |
| Perhydroxyl radical    | 1.70                           |
| Permanganate           | 1.68                           |

As can be seen in Table 5, fluorine is the oxidizing agent with the highest oxidation potential but is not used in advanced oxidation processes technologies due to its high toxicity. For this reason, it is usually used hydroxyl radicals in these processes.

Other characteristics of hydroxyl radicals ( $\cdot\text{OH}$ ) are the rate with which they react in most organic compounds, a behaviour with low selectivity and very short lifetime. For the latter reason, enough amount of hydroxyl radicals ( $\cdot\text{OH}$ ) should be produced during the process. This is achieved using different chemical and photochemical reactions, with individual oxidant or a combination of them, thus assuring a high degradation of the pollutant [29] [30].

Besides, these hydroxyl radicals can attack organic compounds in three different ways: by electron transfer, hydrogen abstraction or radical addition. It is done in one way or another depending on the nature of the organic species. Once complete mineralization of the dyes is achieved, the products obtained are carbon dioxide, water and inorganic ions [30] [33]. Even if there has been colour removal, it is also necessary to follow other parameters such as TOC, BOD, COD or toxicity and thus knowing also the degradation of the possible reaction intermediates.

### 1.5.2. AOPs classification

Advanced oxidation processes can be classified into two large blocks: homogenous processes and heterogeneous processes [25]. Besides, the way to produce hydroxyl radicals ( $\cdot\text{OH}$ ), the generation source of these oxidizing species and the presence or absence of an external energy source allow also classifying the different advanced oxidation processes. Table 6 shows the classification of some AOPs techniques, according to some recently explained aspects [24] [34].

**Table 6.** AOPs classification (Adapted from [24] and [34].)

| <b>Homogeneous processes</b>                 |   |
|--|---|
| <b>a) Without an external energy source</b>  |   |
| Ozonation in alkaline medium.                | $(\text{O}_3/\text{OH}^-)$  |
| Ozonation with hydrogen peroxide.            | $(\text{O}_3/\text{H}_2\text{O}_2)$ ; $(\text{O}_3/\text{H}_2\text{O}_2/\text{OH}^-)$ |
| Fenton.                                      | $(\text{H}_2\text{O}_2/\text{Fe}^{2+})$   |
| <b>b) With an external energy source</b>     |   |
| <b>b1) Energy from ultraviolet radiation</b> | <b>UV</b>   |
| Ozonation and ultraviolet radiation.         | $(\text{O}_3/\text{UV})$  |
| Hydrogen peroxide and ultraviolet radiation. | $(\text{H}_2\text{O}_2/\text{UV})$  |
| Photo-Fenton.                                | $(\text{Fe}^{2+} /\text{H}_2\text{O}_2/\text{UV})$                                    |



|  |  |
|--|--|
| <b>b2) Energy from the ultrasonic source</b> | <b>US</b>                              |
| Ozonation and ultrasounds.                   | (O <sub>3</sub> /US)                   |
| Hydrogen peroxide and ultrasounds.           | (H <sub>2</sub> O <sub>2</sub> /US)    |
| <b>b3) Electrochemical</b>                   |  |
| Electrochemical oxidation                    |  |
| Anodic oxidation.                            |  |
| Electro-Fenton                               |  |
| <b>Heterogeneous processes</b>               |  |
| Catalytic ozonation.                         | (O <sub>3</sub> /Cat.)                 |
| Photocatalytic ozonation.                    | (O <sub>3</sub> /TiO <sub>2</sub> /UV) |
| Heterogeneous photocatalysis.                | (TiO <sub>2</sub> /UV)                 |

### 1.5.3. Advantages and disadvantages of AOPs techniques

The different techniques of advanced oxidation processes used for the elimination of dyes present in textile effluents have both many advantages and some limitations (Table 7).

**Table 7.** Advantages and disadvantages of different AOPs techniques for the elimination of dyes present in textile effluents. (Adapted from [34]).

| Technique | Advantages   | Disadvantages   |
|-----------|--|---|
| Ozone     | The amount of wastewater and sludge is not increased as ozone (O <sub>3</sub> ) can be applied in its gaseous state. | It has a very short lifetime, approximately 20 min. Besides, stability is also affected by the presence of salts, pH and temperature. |

| Technique                         | Advantages  | Disadvantages  |
|-----------------------------------|---|--|
| Fenton                            | It allows COD reduction and an efficient discolouration for soluble and insoluble dyes. Besides, it is easy to implement. | There is sludge production, and the removal is efficient only in a pH value between 2 – 3.5.   |
| H <sub>2</sub> O <sub>2</sub> /UV | There is no sludge generation, and it can achieve partial elimination of COD.   | It is necessary a low pH and to remove suspended solids. This technique is not valid for all types of dyes.  |
| Photochemical                     | There is no sludge generation.  | There is sub-products generation.  |
| Sonolysis                         | There is no excess of sludge production, and no needed to add chemicals.  | Currently, discolouration and mineralization of dyes using sonolysis are not cost-effective. Also, a certain level of dissolved oxygen is required.    |
| Electrochemical                   | The compounds used to degrade are not dangerous and allow an efficient discolouration of soluble and insoluble dyes.      | It can produce sludge, and the effectiveness of the process depends on the character of the dye. Besides, it can also generate high electricity costs. |
| Photocatalysis                    | There is no sludge generation, and it can produce a significant COD reduction.  | There are limitations in the penetration of light.   |

## 2. OBJECTIVES

The main objective of this work is to study the different operational parameters in the abatement process of the indigo carmine dye and methyl orange dye, present in textile effluents, through the different Fenton processes.

To achieve this objective, it has been performed a review of different scientific papers, in which it has been studied and compared the operation variables that affect the efficiency of the degradation process. Besides, it is desired to find the most appropriate operating ranges for the different experimental conditions proposed and to observe the problems or disadvantages that can be originated in each technique. The Fenton techniques studied in these papers are: classical Fenton, Photo-Fenton, Photo-Fenton-Like, Electro-Fenton and Photo-Electro-Fenton.

Besides, it has also been carried out an experimental study, which involves the abatement of an indigo carmine solution through the Photo-Fenton process at circumneutral pH, to assess other conditional factors no evaluated in the literature review papers. The different light sources, the different energy used or the iron precipitation are some examples of these parameters also compared in this work. Besides, based on the results obtained in the experimental part, it will be determined which is the best option for the colour abatement process.



## 3. EVALUATION OF DIFERENT FENTON PROCESSES FOR THE ELIMINATION OF DYES POLLUTANT

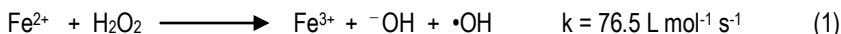
### 3.1. FENTON PROCESSES

Fenton processes are considered a group of advanced oxidation processes (AOPs) techniques very efficient for the degradation of toxic organic compounds with low biodegradability [35]. They are widely used for the advanced treatment of textile effluents as they allow mainly the colour removal of the dyes, due to the high affinity of hydroxyl radicals ( $\cdot\text{OH}$ ) for chromophore groups [31].

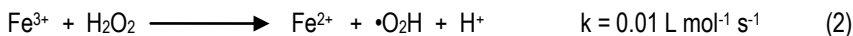
#### 3.1.1. Classical Fenton process

Fenton process was discovered by the British Henry Fenton in 1894 [36]. This process consists basically on the generation of hydroxyl radicals ( $\cdot\text{OH}$ ), at atmospheric pressure and ambient temperature, by combining hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and iron salts, which act as oxidant and catalyst respectively. The classical Fenton reaction is based on a chain radical generation mechanism, formed by the initiation, propagation and termination stages. This process occurs due to electron transfer between the  $\text{Fe}^{2+}$  ions and the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in an aqueous solution in an acid medium [31].

Reaction (1) shows the process of hydroxyl radical formation with its corresponding kinetic constant [35].



The oxidized species  $\text{Fe}^{3+}$  continues reacting with the molecules of hydrogen peroxide, thus generating hydroperoxyl radicals ( $\cdot\text{O}_2\text{H}$ ) and allowing the catalyst reduction to  $\text{Fe}^{2+}$ . This process can be observed in reaction (2), and also its kinetic constant [31].



The comparative between the kinetic constants of the previous reactions, corresponding to the initiation stage, shows that the way of hydroxyl radical generation is much faster than the process of catalyst regeneration. This is because hydroxyl radicals ( $\cdot\text{OH}$ ) oxidizers are much more reactive than hydroperoxyl radicals ( $\cdot\text{O}_2\text{H}$ ).

The main goal of Fenton oxidation is to dissociate hydrogen peroxide into oxygen and water and to transform the dissolved organic carbon into carbon dioxide [36]. This oxidation is affected by some operational parameters such as the concentration of Fenton reagents ( $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ ), the nature of the aqueous matrix, temperature, pollutant concentration and solution pH [37]. This last parameter is one of the most important factors since various studies have shown that the optimal pH range to degrade most organic compounds is between 2.5 – 3.0. Below this pH range, there is a scavenging effect of the hydroxyl radicals by excess  $\text{H}^+$ . By contrast, above this pH value, it is produced the hydrolysis and precipitation of  $\text{Fe}^{3+}$ , thus reducing its catalytic capacity and the global process efficiency [38].

The classical Fenton process has many advantages, such as its operational simplicity, the facility of obtaining and manipulating some reagents, as  $\text{H}_2\text{O}_2$ , and that it does not generate toxic sub-products. However, this process also has some drawbacks, such as the continuous consumption of reagents, the need to control and keep the pH value constant, or the enormous amount of sludge that can be formed [31].

These drawbacks of the classical Fenton method have urged researchers to do some modifications to the conventional process. The most well-known are the Fenton-like process, Photo-Fenton process and Electro-Fenton process [30] [38] [39].

### 3.1.2. Fenton-like process

Fenton-like process is a modification of the classical Fenton process. This process variation differs from its conventional method by the oxidation state of the catalyst used in the reaction. In the Fenton-like process, the catalyst is used in its oxidized form ( $\text{Fe}^{3+}$ ), unlike the conventional method, in which it is used in its reduced form ( $\text{Fe}^{2+}$ ) [30]. A key factor by which the Fenton-like system is used is because  $\text{Fe}^{3+}$  salts have lower costs than  $\text{Fe}^{2+}$  salts [25].

The chain radical generation mechanism that achieves in Fenton-like process starts with the reaction (2), unlike the classical method that begins with the reaction (1) [30]. In the Fenton-like reaction, hydroperoxyl radicals ( $\cdot\text{O}_2\text{H}$ ) are generated, responsible for the oxidation of organic compounds. These radicals have a lower oxidizing capacity than hydroxyl radicals ( $\cdot\text{OH}$ ). For this reason, the mineralization rate in Fenton-like happens slower than in classical Fenton, due to the immediate production of hydroxyl radicals in the Fenton reaction [36].

Besides, several studies have shown that the decay rates of  $\text{H}_2\text{O}_2$  and oxidation of organic complexes are much slower using  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system, than using  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system and are optimal around pH 3 [40] [39] [25].

### 3.1.3. Photo-Fenton process

The Photo-Fenton process consists of the reagents combination of the classical Fenton method and incorporates ultraviolet or solar radiation, of a wavelength between 290 and 400 nm [41]. The use of this radiation increases the efficiency of the pollutant degradation process due to the formation of more hydroxyl radicals ( $\cdot\text{OH}$ ) by two different pathways. For one hand, ultraviolet radiation accelerates the process of reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , thus facilitating the latter's reaction with hydrogen peroxide to generate more hydroxyl radicals ( $\cdot\text{OH}$ ). On the other hand, ultraviolet radiation also improves the photolysis of hydrogen peroxide and thus accelerates the obtaining of hydroxyl radicals ( $\cdot\text{OH}$ ) [31] [41] [42].

Reactions (3) and (4) show the reactions of hydroxyl radical ( $\cdot\text{OH}$ ) generation from the regeneration of  $\text{Fe}^{2+}$  and the photolysis of hydrogen peroxide, respectively [42].

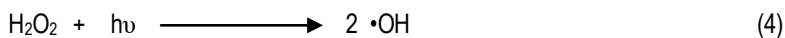
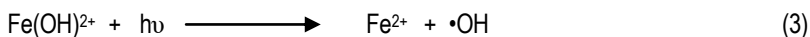


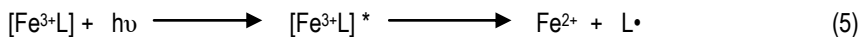
Photo-Fenton process also includes the need to work in a reduced pH range, between 2.8 - 3.5. Operating in this range ensures that the iron species  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  exert their catalytic role and that there is no precipitation of inactive iron oxyhydroxides [43]. However, working under these optimal conditions, with an acid pH, can make the process unattractive for large-scale application.

Several studies have shown that light intensity has a significant effect on reaction result [41]. Depending on the light source used, the Photo-Fenton (Ph-F) process can be classified as Ph-F solar process or Ph-F artificial UV process. The Black Light Blue (BLB) lamps, the LEDs and the mercury lamps are some examples of ultraviolet light sources used during the last years in the Photo-Fenton process on an industrial scale.

### 3.1.4. Photo-Fenton process at neutral pH

As mentioned above, the need previously to acidify the solution and then neutralize it for reuse, after performing Photo-Fenton treatment, causes an increase in operational costs [44]. The possibility of working at neutral pH or near neutral values using the Photo-Fenton process has generated a prominent interest in the research community [43].

The problems associated with the inefficiency of the Photo-Fenton process at a neutral pH can be solved by the addition of stable compounds, able to form complexes with iron [45]. These stable compounds are called chelating agents and are capable of producing photoactive species ( $\text{Fe}^{3+}\text{L}$ ), which can maintain dissolved iron and avoid the iron oxyhydroxides precipitation [46]. Besides, these photoactive species have to absorb UV-VIS light and to undergo photochemical reductions to obtain  $\text{Fe}^{2+}$  ions, as seen in the reaction (5) [43]. The  $\text{Fe}^{2+}$  ions react with hydrogen peroxide through the reaction (1), thus generating hydroxyl radicals, which are responsible for destroying the persistent pollutants.



In general, chelating agents must be highly stable, environmentally friendly, highly biodegradable and non-toxic [46]. Some of the best known chelating agents used in Photo-Fenton process to operate at neutral pH are oxalate, Ethylenediaminetetraacetic acid (EDTA), Ethylenediamine-N,N'-disuccinic acid (EDDS) and Diethylenetriaminepentaacetic acid (DTPA). The main application of the latter is in agriculture and horticulture, such as organic fertilizer [47].

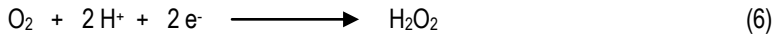
### 3.1.5. Electro-Fenton process

Electro-Fenton process is a modification of the classical Fenton method, and it also allows an effective colour removal and destruction of molecules of contaminants present in wastewater



[48]. This process is based on the electrocatalytic generation of the Fenton reagents, through the use of compressed air and the external addition of catalyst at low concentration [49].

H<sub>2</sub>O<sub>2</sub> is produced in a carbonaceous cathode by a reduction reaction using oxygen dissolved in an acidic environment [48]. Graphite, carbon felt, reticulated vitreous carbon or gas diffusion electrodes are examples of the most commonly used carbonaceous cathodes in the Electro-Fenton process [50]. Reaction (6) shows the H<sub>2</sub>O<sub>2</sub> generation reaction from oxygen reduction [48] [49] [50] [51] [52].

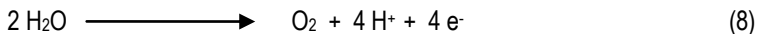


The addition of a specified amount of catalyst (Fe<sup>2+</sup>), to the acid solution, improves the oxidation capacity of H<sub>2</sub>O<sub>2</sub> and, the Fenton reaction described in reaction (1) is achieved, thereby generating Fe<sup>3+</sup> ions and hydroxyl radicals (·OH) [50]. These radicals are necessary because they can react with organic compounds and obtain their complete mineralization [48].

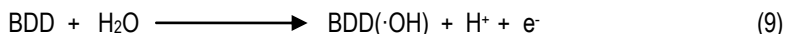
Fe<sup>3+</sup> ions produced in the Fenton reaction can be quickly regenerated to Fe<sup>2+</sup> by an electrochemical reduction produced in the cathode. This advantage of Electro-Fenton process allows an increase in the rate of organic pollutant destruction [52] [50]. Reaction (7) shows the regeneration of the catalyst from the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> [48] [50] [52].



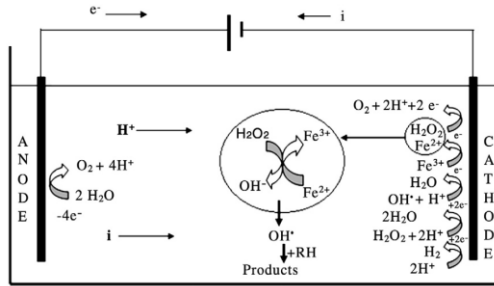
The molecular oxygen required to produce H<sub>2</sub>O<sub>2</sub> in the cathode is generated from the water oxidation at the anode, as shown in reaction (8) [48].



The choice of the anode and cathode material is a very important decision in the Electro-Fenton process (Figure 3) since an unstable selection of the anode, for example, could cause a deterioration of electrode in electrolytic cells [51]. Two of the most commonly used anodes for the wastewater treatment using Electro-Fenton process are platinum (Pt) and boron-doped diamond (BDD) [52]. BDD anode has a high O<sub>2</sub> overpotential, which encourages the formation of many hydroxyl radicals on its surface (BDD (·OH)) and allows to improve the efficiency of the Electro-Fenton process. Reaction (9) shows the generation reaction of hydroxyl radicals formed on the BDD anode surface [50] [49].



The efficiency of Electro-Fenton process depends mainly on temperature, pH, the nature of the electrode, electrolytes, catalyst concentration, dissolved oxygen level and current density [53].



**Figure 3.** Reaction mechanism of Electro-Fenton process (Figure taken from [51]).

The fact that non-toxic products are used or generated makes it possible to classify the Electro-Fenton process as an environmentally friendly method for wastewater treatment. Other aspects to consider in Electro-Fenton process are the high reaction efficiency obtained, and the fact that it is an economical process because it uses electricity as a clean energy source [51] [48].

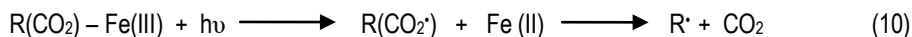
### 3.1.6. Photo-Electro-Fenton process

Photo-Electro-Fenton process is a modification of the classical method based on the combination of the Electro-Fenton process and ultraviolet (UV) radiation. This new method, in which the reaction content is exposed to ultraviolet radiation, is used successfully for wastewater treatments [54].

The incorporation of ultraviolet radiation into this method allows solving the Electro-Fenton process problem, which consists basically in the difficulty of destroying Fe(III)-carboxylates complexes through hydroxyl radicals ( $\cdot\text{OH}$ ) [55].

Photo-Electro-Fenton process improves the regeneration of the  $\text{Fe}^{2+}$  catalyst and increases the production of hydroxyl radicals ( $\cdot\text{OH}$ ) by photoreduction of  $\text{Fe}(\text{OH})^{2+}$ , following the reaction (3) [55]. Besides, both the  $\text{Fe}^{3+}$  complexes photoactivation and the  $\text{Fe}^{2+}$  production, due to the photolysis of these complexes, produce an improvement in Photo-Electro-Fenton systems

efficiency [53] [54]. Reaction (10) shows the process of photo-decarboxylation of oxalic acids, which behave as photoactive complexes in the presence of ferric ions, in an acid medium [53] [54].



However, the Photo-Electro-Fenton process also has some limitations. The need to acidify effluents for treatment, in a pH range between 2.8 – 3.5, or the high electrical cost of UV radiation lamps represent these disadvantages for applying this process at industrial scale [56].

### 3.2. FENTON PROCESSES: BENEFITS AND DRAWBACKS

Table 8 shows a summary of the main benefits and limitations of different Fenton methods, explained recently, highlighting some strengths and weaknesses of each technique.

**Table 8.** Benefits and drawbacks of the different Fenton techniques. (Own elaboration).

| Fenton technique | Benefits   | Drawbacks   | References |
|------------------|--|---|------------|
| Classical Fenton | <ul style="list-style-type: none"> <li>- P and T ambient operation.</li> <li>- Simple to implement.</li> <li>- Low – toxicity.</li> </ul>  | <ul style="list-style-type: none"> <li>- High operational costs.</li> <li>- Need to acidify the solution.</li> <li>- Generation of large volumes of iron sludge.</li> </ul>   | 36         |
| Fenton-Like      | <ul style="list-style-type: none"> <li>- Use of <math>\text{Fe}^{3+}</math> ions as the catalyst, more economical than <math>\text{Fe}^{2+}</math> ions.</li> </ul>  | <ul style="list-style-type: none"> <li>- Rate of <math>\text{H}_2\text{O}_2</math> decomposition and oxidation rate of organic compounds are much slower.</li> <li>- Need of previously acidifying the medium.</li> </ul> | 25, 39     |
| Photo-Fenton     | <ul style="list-style-type: none"> <li>- Increase in the regeneration rate of <math>\text{Fe}^{2+}</math> catalyst by photoreduction of <math>\text{Fe}^{3+}</math>.</li> <li>- Generation of more <math>\cdot\text{OH}</math> by direct photolysis of <math>\text{H}_2\text{O}_2</math>.</li> </ul> | <ul style="list-style-type: none"> <li>- Need to operate in a narrow pH range (between 2.8 – 3.5).</li> <li>- Generates high investment, maintenance and electrical costs of UV lamps.</li> </ul>                         | 57, 43, 31 |

| Fenton technique           | Benefits  | Drawbacks   | References |
|----------------------------|---|---|------------|
| Photo-Fenton at neutral pH | <ul style="list-style-type: none"> <li>- Work at different pH values.</li> <li>- Catalyst can be reused.</li> <li>- Low formation of iron hydroxide sludge.</li> </ul>  | <ul style="list-style-type: none"> <li>- Low process efficiency with a bad choice of the chelating agent.</li> <li>- Besides, it could increase the TOC to remove and the total cost of the process.</li> </ul> | 41         |
| Electro-Fenton             | <ul style="list-style-type: none"> <li>- Environmentally friendly.</li> <li>- Continuous Fe<sup>2+</sup> regeneration.</li> <li>- Generates an 80% cost reduction due to the in situ H<sub>2</sub>O<sub>2</sub> electrogeneration.</li> </ul> | <ul style="list-style-type: none"> <li>- Requirement of acidifying the medium.</li> <li>- Some intermediates can considerably inhibit mineralization.</li> </ul>  | 37, 48, 56 |
| Photo-Electro-Fenton       | <ul style="list-style-type: none"> <li>- Photoreduction of Fe(OH)<sup>2+</sup> species and photodecarboxylation of Fe(III) carboxylate species, using UVA or UVB radiation.</li> </ul>  | <ul style="list-style-type: none"> <li>- High electrical cost associated with the artificial UV lamps.</li> <li>- Limitations to previously acidify the effluents.</li> </ul>                                   | 56         |

## 4. REVIEW OF THE OPTIMAL PARAMETERS OF DIFFERENT FENTON TECHNIQUES

The results presented in this chapter are the summary of a bibliographic study. It has focused on studying the different operational parameters that affect to various Fenton processes, using the indigo carmine or the methyl orange as dyes to degrade. This part studies the degradation of these pollutants present in textile industry wastewater, focusing mainly on achieving a high elimination of both colour and TOC.

### 4.1. EVALUATION OF OPERATIONAL PARAMETERS IN THE CLASSICAL FENTON PROCESS

N.A. Youssef *et al.* (2016) studied the oxidation of the methyl orange (MO) dye through the classical Fenton process, at room laboratory temperature and atmospheric pressure. They focused on optimizing the different system parameters and thus studying the influence of the dosage of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$ , initial methyl orange concentration and the effect of pH, among others.

According to N.A. Youssef *et al.* (2016), an important effect on the degradation efficiency of methyl orange dye can be observed by varying the initial dosage of  $\text{H}_2\text{O}_2$  from  $1.18 \times 10^{-3}$  to  $3.4 \times 10^{-2}$  M, under the following experimental conditions:  $[\text{Fe}^{2+}] = 1.9 \times 10^{-4}$  M,  $[\text{MO}] = 5.4 \times 10^{-5}$  M, pH = 6.69 (Figure 4).

N.A. Youssef *et al.* (2016) concluded that the optimal initial concentration value of  $\text{H}_2\text{O}_2$ , for the experimental conditions proposed, is  $2.93 \times 10^{-3}$  M, obtaining a methyl orange degradation of 86.25%, in 15 minutes of reaction. Besides, they also verified that for the same reaction time, using a lower initial concentration of  $\text{H}_2\text{O}_2$ , exactly  $1.18 \times 10^{-3}$  M, the degradation of methyl orange dye achieved was 77.5%, while for a higher initial concentration of  $\text{H}_2\text{O}_2$ , of  $3.4 \times 10^{-2}$  M, they obtained only 45.65% degradation [58].

Another critical parameter in the Fenton process is the initial concentration of  $\text{Fe}^{2+}$  employed. In the study conducted by N.A. Youssef *et al.* (2016), the effect of the  $\text{Fe}^{2+}$  dosage on the methyl orange dye degradation was also studied. They decided to vary the initial concentrations of  $\text{Fe}^{2+}$  from  $3.5 \times 10^{-5}$  to  $1.9 \times 10^{-4}$  M, under the following experimental conditions:  $[\text{H}_2\text{O}_2] = 2.93 \times 10^{-3}$  M,  $[\text{MO}] = 5.4 \times 10^{-5}$  M,  $\text{pH} = 6.69$  (Figure 5).

The experiments carried out by N.A. Youssef *et al.* (2016), allowed them to conclude that for these experimental conditions, the optimal initial  $\text{Fe}^{2+}$  application was the higher amount, namely  $1.9 \times 10^{-4}$  M, achieving a dye degradation of 90.12%. By contrast, using a lower initial concentration of  $\text{Fe}^{2+}$ , exactly  $3.5 \times 10^{-5}$  M, they obtained only 27.59% of degradation [58].

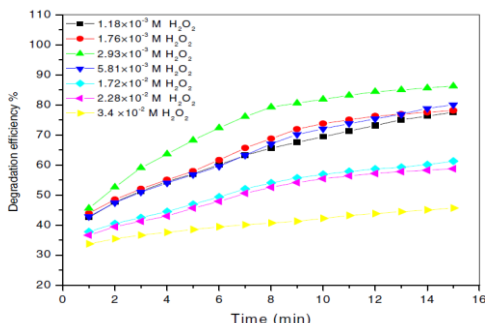
Different concentrations of methyl orange dye were also studied by N.A. Youssef *et al.* (2016), and tested for their influence on the effectiveness of dye degradation by the Fenton process. They chose to vary the concentration values of MO from  $2.7 \times 10^{-5}$  to  $1.08 \times 10^{-4}$  M, under the following experimental conditions:  $[\text{H}_2\text{O}_2] = 2.93 \times 10^{-3}$  M,  $[\text{Fe}^{2+}] = 1.9 \times 10^{-4}$  M,  $\text{pH} = 6.69$  (Figure 6).

N.A. Youssef *et al.* (2016) concluded from the experimental results, that in 15 minutes of reaction, employing an initial methyl orange application of  $1.08 \times 10^{-4}$  M, it can be achieved a degradation of 84.13%. In contrast, for a lower methyl orange concentration, exactly of  $2.7 \times 10^{-5}$  M, they obtained a better degradation of pollutant, more specifically 91.12% degradation.

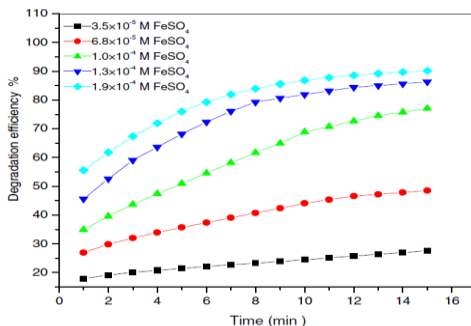
Finally, the effect of the initial pH of the solution is another aspect that has been studied by N.A. Youssef *et al.* (2016). They decided to vary the pH range between 2.79 - 8, under the following experimental conditions:  $[\text{H}_2\text{O}_2] = 2.93 \times 10^{-3}$  M,  $[\text{Fe}^{2+}] = 1.9 \times 10^{-4}$  M,  $[\text{MO}] = 5.4 \times 10^{-5}$  M (Figure 7).

In 15 minutes of reaction, using a pH value of 2.79, N.A. Youssef *et al.* (2016) reached a 97.8% degradation of the methyl orange dye. In contrast, using a pH value of 6.69, they also achieved noteworthy degradation, more specifically 90.12% degradation.

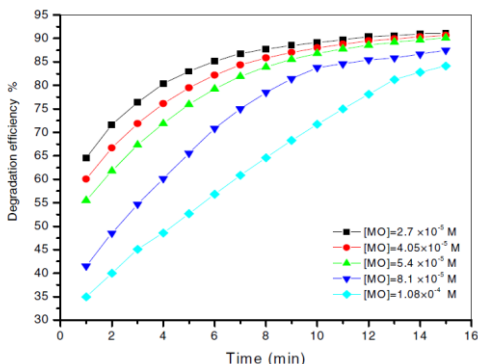
Based on the results obtained by N.A. Youssef *et al.* (2016), it can be concluded that an optimum operation ratio of  $\text{MO}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ , to degrade a solution of methyl orange dye through the Fenton technique, is approximately 1/108 and 1/15, respectively.



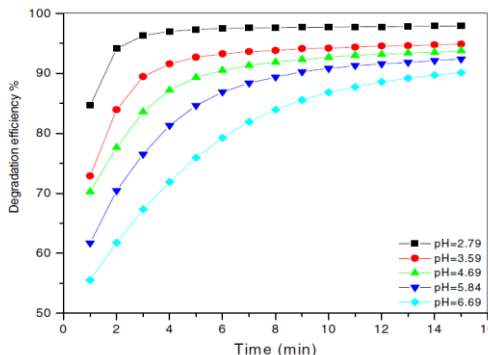
**Figure 4.** Effect of  $[H_2O_2]$  on the degradation of MO by Fenton reaction. Experimental conditions:  $[MO] = 5.4 \times 10^{-5} \text{ M}$ ;  $[Fe^{2+}] = 1.9 \times 10^{-4} \text{ M}$ ;  $\text{pH} = 6.69$ ; (Figure taken from N.A. Youssef *et al.*, 2016).



**Figure 5.** Effect of  $[Fe^{2+}]$  on the degradation of MO by Fenton reaction. Experimental conditions:  $[MO] = 5.4 \times 10^{-5} \text{ M}$ ;  $[H_2O_2] = 2.93 \times 10^{-3} \text{ M}$ ;  $\text{pH} = 6.69$ ; (Figure taken from N.A. Youssef *et al.*, 2016).



**Figure 6.** Effect of the concentration of MO on the degradation by Fenton reaction. Experimental conditions:  $[H_2O_2] = 2.93 \times 10^{-3} \text{ M}$ ;  $[Fe^{2+}] = 1.9 \times 10^{-4} \text{ M}$ ;  $\text{pH} = 6.69$ ; (Figure taken from N.A. Youssef *et al.*, 2016).



**Figure 7.** Effect of initial pH on the degradation of MO by Fenton reaction. Experimental conditions:  $[MO] = 5.4 \times 10^{-5} \text{ M}$ ;  $[H_2O_2] = 2.93 \times 10^{-3} \text{ M}$ ;  $[Fe^{2+}] = 1.9 \times 10^{-4} \text{ M}$ ; (Figure taken from N.A. Youssef *et al.*, 2016).

## 4.2. EVALUATION OF OPERATIONAL PARAMETERS IN THE PHOTO-FENTON PROCESS

There are some papers which compare different amounts of  $H_2O_2$  and dosages of  $Fe^{2+}$  employed, under different experimental conditions, to degrade the indigo carmine (IC) dye through the Photo-Fenton process. The studies of Mahakulkar, S. *et al.* (2019) and de Oliveira Ramos, R. *et al.* (2019) are some examples of these papers.

Mahakulkar, S. *et al.* (2019) studied the Photo-Fenton process for the degradation of indigo carmine dye in a laboratory-scale photo reactor. Their study focused on testing different volumes and concentrations of  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$ , keeping the dye concentration and pH of the solution constant in  $1.25 \times 10^{-4}$  M and 3.5, respectively. Besides, the experiments done by Mahakulkar, S. *et al.* (2019) were carried out in an 800 mL reactor and were exposed to monochromatic ultraviolet light of 8 W of power, and 254 nm of wavelength.

Firstly, Mahakulkar, S. *et al.* (2019) decided to keep constant the amount of  $\text{FeSO}_4$  at a value of 2 mL ( $10^{-2}$  M) and to vary only the initial  $\text{H}_2\text{O}_2$  (30% w/v) concentration between 4.41 - 13.24 mM (Table 9). For the experimental conditions of their study, they proved that the optimal value of  $\text{H}_2\text{O}_2$  was 7.06 mM, thus achieving a degradation of indigo carmine dye of 98.16%, and with a reaction rate of  $0.5 \times 10^{-5}$  mol/(L·min) [59]. Besides, according to Mahakulkar, S. *et al.* (2019), working with 4.41 mM of  $\text{H}_2\text{O}_2$  would lead to a significant decrease in the degradation of indigo carmine dye, namely 51.14% degradation.

**Table 9.** Percentage degradation of IC dye to different  $\text{H}_2\text{O}_2$  concentrations through the Photo-Fenton process. Experimental conditions:  $[\text{IC}] = 1.25 \times 10^{-4}$  M; pH = 3.5;  $\text{FeSO}_4 = 2$  mL ( $10^{-2}$  M) (Table adapted from Mahakulkar, S. *et al.* (2019)).

| $\text{H}_2\text{O}_2$ [mM] | % IC Degradation | Rate of reaction $\times 10^{-5}$ [mol/(L·min)] |
|-----------------------------|------------------|---|
| 13.24                       | 64.11            | 0.3   |
| 8.82                        | 95.42            | 0.2   |
| 7.06                        | 98.16            | 0.5   |
| 4.41                        | 51.14            | 0.4   |

Once they obtained the optimal value of  $\text{H}_2\text{O}_2$ , Mahakulkar, S. *et al.* (2019) decided then to keep it constant and to vary only the volume of  $\text{FeSO}_4$  ( $10^{-2}$  M), between the values of 1.5 - 2.5 mL (Table 10). The results obtained allowed them to conclude that for their experimental conditions, the optimal amount of  $\text{FeSO}_4$  is 2 mL since degradation of the indigo carmine dye is 98.04% and its reaction rate of  $0.5 \times 10^{-5}$  mol/(L·min) [59]. According to Mahakulkar, S. *et al.* (2019), the addition of 2.5 mL of  $\text{FeSO}_4$ , only 0.5 mL more of  $\text{FeSO}_4$  than the optimal, would result in a significant decrease in the degradation of indigo carmine, as it would degrade only 32.8%.



**Table 10.** Percentage degradation of the IC dye to different  $\text{FeSO}_4$  ( $10^{-2}$  M) volumes through the Photo-Fenton process. Experimental conditions:  $[\text{IC}] = 1.25 \times 10^{-4}$  M;  $\text{pH} = 3.5$ ;  $[\text{H}_2\text{O}_2] = 7.06$  mM (Table adapted from Mahakulkar, S. et al. (2019)).

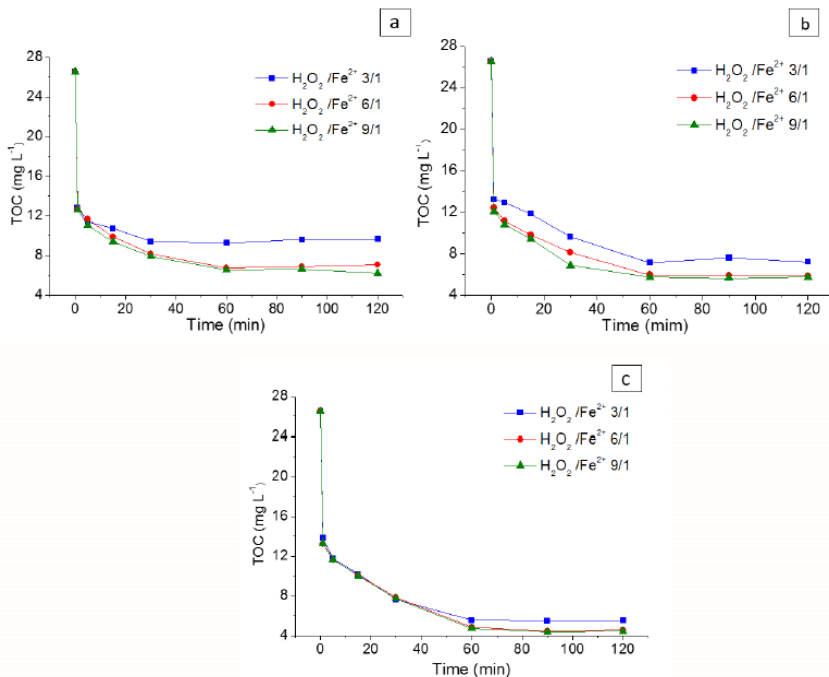
| $\text{FeSO}_4$ [mL] | % IC Degradation | Rate of reaction $\times 10^{-5}$ [mol/(L·min)] |
|----------------------|------------------|---|
| 1.5                  | 79.9             | 0.4   |
| 2                    | 98.04            | 0.5   |
| 2.5                  | 32.8             | 0.3   |

Another study that has also examined the independent variables that affect to the degradation of indigo carmine through the process Photo-Fenton is the one that was carried out by de Oliveira Ramos, R. *et al.* (2019). According to their study, the experiments were carried out on a 1.5 L tubular FP reactor, equipped with a mercury vapour UV-C lamp, of 254 nm wavelength and 90 W power supply. Besides, it was also operated with recirculation of 10 L of 50 ppm indigo carmine dye and a constant pH value of 3 [60]. The work performed by de Oliveira Ramos, R. *et al.* (2019) focused mainly on using and comparing three different dosages of  $\text{Fe}^{2+}$  and proportions of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  to find the optimal values in the conditions proposed for the degradation of indigo carmine (Table 11).

**Table 11.** Dosages of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  proportions used in their experiments. (Table from de Oliveira Ramos, R. *et al.* (2019)).

|  | Level |        |      |
|--|-------|--------|------|
|  | Low   | Center | High |
| $\text{Fe}^{2+}$ dosage [mM]                       | 2     | 4      | 8    |
| $\text{H}_2\text{O}_2 / \text{Fe}^{2+}$ proportion | 3/1   | 6/1    | 9/1  |

Figure 8 shows the experimental results obtained by the study of de Oliveira Ramos, R. *et al.* (2019) for the different dosages of  $\text{Fe}^{2+}$  and proportions of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  employed, mentioned in Table 11. The Figure 8.a., Figure 8.b. and Figure 8.c. correspond to a dosage of  $\text{Fe}^{2+}$  of 2, 4 and 8 mM respectively.



**Figure 8.** TOC variation over time for different dosages of Fe<sup>2+</sup>. (a) [Fe<sup>2+</sup>] = 2 mM, (b) [Fe<sup>2+</sup>] = 4 mM, (c) [Fe<sup>2+</sup>] = 8 mM. (Figure taken from de Oliveira Ramos, R. *et al.* (2019)).

According to de Oliveira Ramos, R. *et al.* (2019), the oxidation reaction of indigo carmine dye takes place in two steps, one rapid, from 0 to 1 minute, and one slow, from 1 to 60 minutes. After 60 minutes of reaction, the variation of TOC remains practically constant. Besides, as can be observed from the experimental results performed by de Oliveira Ramos, R. *et al.* (2019), at higher dosages of Fe<sup>2+</sup>, higher reduction of TOC removal is obtained and consequently, a higher degradation of indigo carmine dye. Similarly, for the three dosages of Fe<sup>2+</sup> employed, at higher proportions of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, higher degradations of indigo carmine dye are also obtained.

Finally, after performing an analysis of variance, de Oliveira Ramos, R. *et al.* (2019) concluded that the dosage of Fe<sup>2+</sup> on the reaction rate constant is more influential than the dosage of H<sub>2</sub>O<sub>2</sub>. They suggested that this is because, on the Photo-Fenton process the production of hydroxyl radicals ( $\cdot\text{OH}$ ) by direct H<sub>2</sub>O<sub>2</sub> photolysis is less significant than the formation of the same radicals using reactions catalysed directly by the iron species [60].

### 4.3. EVALUATION OF OPERATIONAL PARAMETERS IN THE PHOTO-FENTON-LIKE PROCESS

As explained above, the Photo-Fenton-Like process is based on the combination of ultraviolet radiation and  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ . Some studies have also focused on studying the efficiency of the different operational parameters of this technique, using the indigo carmine dye (Mahakulkar, S. *et al.* (2019)) or the methyl orange dye (Devi, L.G. *et al.* (2010)) as colourants to degrade.

In the study performed by Devi, L.G. *et al.* (2010), the effect of the initial pH of the solution, the initial concentration of methyl orange and the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions concentration were tested for the degradation of the methyl orange dye, through Photo-Fenton-Like process. In these experiments, a total of 200 mL of solution were treated under different experimental conditions in a reactor and were directly exposed to radiation from a mercury vapour lamp, with an average pressure of 125 W [61].

First, Devi, L.G. *et al.* (2010) started studying the influence of initial pH on the discolouration of methyl orange dye. Some experiments were performed at different pH values, between 1.2 - 9.5, under the following experimental conditions:  $[\text{Fe}^{3+}] = 6$  ppm,  $[\text{H}_2\text{O}_2] = 10$  ppm, and  $[\text{MO}] = 10$  ppm. According to Devi, L.G. *et al.* (2010), at pH = 1.2, the degradation rate of methyl orange dye is reduced due to the excess of  $\text{H}^+$  ions, which act as hydroxyl radical scavengers. Besides, at pH value of 1.2 they obtained the only discolouration of approximately 60%. Instead, working at a pH value around 3, they obtained a complete discolouration of the methyl orange dye. According to Devi, L.G. *et al.* (2010), this is because half of the irons species exists as  $\text{Fe}^{3+}$  ions, while the other half exist as complexes  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ , which are photoactive species capable of producing hydroxyl radicals along with the regeneration of  $\text{Fe}^{2+}$  ions [61]. At higher pH values, they obtained a decrease in the rate of degradation and a lower discolouration of the methyl orange dye, due to the precipitation of iron ions in the form of oxyhydroxides.

Another factor that was also studied by Devi, L.G. *et al.* (2010) was the effect of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions. According to them, the speed constant calculated for the Photo-Fenton-Like process is 4.6 times higher than for the Photo-Fenton process, even though the speed constant for the Fenton-Like process, without UV radiation, is lower than for the classical Fenton method [61].

Finally, Devi, L.G. *et al.* (2010) also analysed the effect of the initial concentration of dye for the degradation of methyl orange dye through Photo-Fenton-Like process. They decided to vary the initial methyl orange dye concentration between 10, 15 and 20 ppm, keeping the other parameters constant, namely the  $\text{Fe}^{3+}$  concentration, the  $\text{H}_2\text{O}_2$  content and the initial pH of the solution. As experimental results, they obtained that for initial methyl orange concentrations of 10, 15 and 20 ppm, it had been discoloured by 100%, 76% and 60%, respectively [61]. According to Devi, L.G. *et al.* (2010), this decrease in discolouration efficiency is in part because photons cannot enter the solution due to a large amount of dye present.

Concerning the indigo carmine dye, the abovementioned study performed by Mahakulkar, S. *et al.* (2019) also carried out different experiments to determine in this case the optimal volume of  $\text{FeCl}_3$  and concentration of  $\text{H}_2\text{O}_2$  required to degrade the dye, through the Photo-Fenton-Like process. Their investigations were also carried out in an 800 mL reactor, with an initial concentration of indigo carmine dye of  $1.25 \times 10^{-4}$  M and a pH value of 3.5. Besides, the solution was exposed to monochromatic ultraviolet light of 8 W of power and a 254 nm wavelength [59].

First, Mahakulkar, S. *et al.* (2019) decided to keep constant the volume of  $\text{FeCl}_3$  ( $10^{-2}$  M) solution, with a value of 2 mL, and to modify only the amount of  $\text{H}_2\text{O}_2$  (30% w/v) to be added, between 7.06 – 17.65 mM (Table 12). Their experimental results show that the optimal value of  $\text{H}_2\text{O}_2$  to be added is 8.82 mM since it achieves a degradation of the indigo carmine dye of 98.47% and a reaction rate of  $0.3 \times 10^{-5}$  mol/(L·min).

**Table 12.** Percentage degradation of the IC dye to different  $\text{H}_2\text{O}_2$  concentrations through the Photo-Fenton-Like process. Experimental conditions:  $[\text{IC}] = 1.25 \times 10^{-4}$  M; pH = 3.5;  $\text{FeSO}_4 = 2$  mL ( $10^{-2}$  M) (Table adapted from Mahakulkar, S. *et al.* (2019)).

| $\text{H}_2\text{O}_2$ [mM] | % IC Degradation | Rate of reaction $\times 10^{-5}$ [mol/(L·min)] |
|-----------------------------|------------------|---|
| 17.65                       | 80.48            | 0.08  |
| 13.24                       | 96.86            | 0.2   |
| 8.82                        | 98.47            | 0.3   |
| 7.06                        | 95.26            | 0.3   |

Once Mahakulkar, S. *et al.* (2019) found the optimal concentration value of  $\text{H}_2\text{O}_2$  for the proposed experimental conditions; they kept it constant and decided to vary then the amount of  $\text{FeCl}_3$ . The different  $\text{FeCl}_3$  ( $10^{-2}$  M) values they treated with 8.82 mM of  $\text{H}_2\text{O}_2$  were 1, 2 and 3 mL, as shown in Table 13. The best result they obtained was the experiment in which they employed 2 mL of  $\text{FeCl}_3$  since they achieve a degradation of the indigo carmine dye of 77.72% and a reaction rate of  $0.3 \times 10^{-5}$  mol/(L·min) [59]. Instead, for 1 and 3 mL volumes of  $\text{FeCl}_3$  ( $10^{-2}$  M), they only achieved a 67.77% and 31.82% degradation of the dye respectively.

**Table 13.** Percentage degradation of the IC dye to different  $\text{FeCl}_3$  ( $10^{-2}$  M) volumes through the Photo-Fenton-Like process. Experimental conditions:  $[\text{IC}] = 1.25 \times 10^{-4}$  M;  $\text{pH} = 3.5$ ;  $[\text{H}_2\text{O}_2] = 8.82$  mM (Table adapted from Mahakulkar, S. *et al.* (2019)).

| $\text{FeCl}_3$ [mL] | % IC Degradation | Rate of reaction $\times 10^{-5}$ [mol/(L min)] |
|----------------------|------------------|---|
| 1                    | 67.77            | 0.03  |
| 2                    | 77.72            | 0.3   |
| 3                    | 31.82            | 0.2   |

#### 4.4. EVALUATION OF OPERATIONAL PARAMETERS IN THE ELECTRO-FENTON PROCESS

A study not so recent but also considered essential to take into account is that carried out by Flox, C. *et al.* (2006). In their research, they made a comparison between the different anodes used in Electro-Fenton treatments, to degrade aqueous acid solutions containing up 900 ppm of indigo carmine dye and 0.05 M  $\text{Na}_2\text{SO}_4$ . Besides, Flox, C. *et al.* (2006) also examined the influence of  $\text{Fe}^{2+}$  concentration, the effect of pH, current density and dye concentration, among other aspects.

The experiments performed by Flox, C. *et al.* (2006) were carried out in an open, one-compartment and thermostated cylindrical glass cell containing a 100 mL solution stirred with a magnetic bar [62]. The anode they used was a 3 cm<sup>2</sup> Pt foil of 99.99% purity or a 3 cm<sup>2</sup> BDD film deposited on a conductive Si sheet. About the cathode, in all experiments, they used a 3 cm<sup>2</sup> carbon-PTFE electrode, fed with pure oxygen at constant flow [62].

First, Flox, C. *et al.* (2006) decided to evaluate the efficiency of the two different anodes used in the Electro-Fenton process to degrade indigo carmine dye and, to compare the elimination of TOC achieved with each other. The experimental conditions proposed were to treat 100 mL of an indigo carmine solution with a concentration of 220 ppm in 0.05 M Na<sub>2</sub>SO<sub>4</sub>, with an initial pH value of 3, a temperature of 35 °C, a current density of 33 mA·cm<sup>-2</sup> and a Fe<sup>2+</sup> concentration of 1 mM [62]. In both trials, they achieved a complete discolouration in less than 10 minutes. However, they obtained a different degradation depending on the anode used. Their results allowed them to conclude that for the same reaction time, namely 9 hours, the TOC reduction achieved using the Pt anode was only 49%, while for the BDD anode they obtained a degradation of 91% [62]. According to Flox, C. *et al.* (2006), the low mineralization of indigo carmine dye in the Electro-Fenton process with Pt anode could be due to the formation of some products, such as Fe<sup>3+</sup> complexes, which cannot be oxidized by hydroxyl radicals. The fact that with the BDD anode a higher degradation is obtained is partly due to the higher amount of hydroxyl radicals produced on its surface, and consequently to the higher organic matter destruction [62].

Because Flox, C. *et al.* (2006) obtained better results operating with the BDD anode, they decided to carry out the following experiments with this type of anode. In some trials they performed, they chose to vary only the Fe<sup>2+</sup> concentration, between the values of 0.20 - 5.0 mM, and they kept the other parameters constant. They observed that for the different experiments, the TOC removal obtained was between 91 - 95%. According to Flox, C. *et al.* (2006), the oxidizing power of Electro-Fenton method with BDD anode is practically independent of the Fe<sup>2+</sup> amount.

Another factor evaluated in the study performed by Flox, C. *et al.* (2006) is the current density. They executed the Electro-Fenton process for the degradation of indigo carmine dye, modifying current density between 33, 100 and 150 mA·cm<sup>-2</sup>. Besides, the experimental conditions employed were as follows: 100 mL of indigo carmine solution with an initial concentration of 200 ppm, at a pH value of 3 and a Fe<sup>2+</sup> concentration of 1 mM [62]. The experimental results allowed them to prove that working with a current density of 150 mA·cm<sup>-2</sup>, complete mineralization of the indigo carmine dye was achieved in a shorter time. However, there was also an increase in specific charge consumption [62]. According to Flox, C. *et al.*

(2006), the improvement in mineralization because of the rise of current density is due in part to the high hydroxyl radicals production by both the anode and the cathode.

Lastly, the influence of indigo carmine concentration was another parameter also discussed in the study of Flox, C. *et al.* (2006). They decided to vary the initial dye concentration between the following values: 112, 220, 440 and 881 ppm. Besides, they also employed a BDD anode with a  $\text{Fe}^{2+}$  concentration of 1 mM. After one hour of treatment, the highest degradation they achieved was 54%, using 112 ppm as the initial concentration of indigo carmine. For higher values of indigo carmine concentration, they obtained dwindling TOC removal, as can be observed in Table 14 [62]. This decrease in TOC reduction may be due, among other things, to the lack of oxidizing agents, required to eliminate the high indigo carmine amount present in the solution, since the operation ratio of  $\text{Fe}^{2+}/\text{IC}$  for this latter part is 1/112.

**Table 14.** Percentage of removed TOC with increasing IC concentration through Electro-Fenton process with a BDD anode and 1.0 mM  $\text{Fe}^{2+}$ . (Source: prepared by author based on results of [62])

| IC concentration [ppm] | % TOC removal |
|------------------------|---------------|
| 112                    | 54            |
| 220                    | 52            |
| 440                    | 47            |
| 881                    | 41            |

#### 4.5. EVALUATION OF OPERATIONAL PARAMETERS IN THE PHOTO-ELECTRO-FENTON PROCESS

The study explained above, and carried out by Flox, C. *et al.* (2006) also focused on investigating the influence of some parameters for the degradation of indigo carmine dye through the Photo-Electro-Fenton process. Besides, the paper by Enric Brillas (2014) focused on explaining, among other aspects, the different results obtained in the study by Flox, C. *et al.* (2006), in which he also took part.

The work performed by Flox, C. *et al.* (2006) used the Photo-Electro-Fenton process to also treat 100 mL of indigo carmine solution with an initial concentration of 220 ppm, at a pH value of

3, with a current density of  $33 \text{ mA}\cdot\text{cm}^{-2}$  and a  $\text{Fe}^{2+}$  concentration of  $1 \text{ mM}$  [62]. The modifications made from the Electro-Fenton process were the incorporation of a UVA radiation of  $6 \text{ W}$  of power, and the use of a  $3 \text{ cm}^2$  Pt anode. The TOC reduction obtained by Flox, C. *et al.* (2006) in the Photo-Electro-Fenton process with a Pt anode and a  $\text{Fe}^{2+}$  concentration of  $1 \text{ mM}$  was  $84\%$ , in a reaction time of 9 hours. According to Enric Brillas (2014), the most persistent products in the medium are Fe(III)-oxalate and Fe(III)-oxamate complexes. The Fe(III)-oxalate complex disappears in a reaction time of 480 minutes, while the Fe(III)-oxamate complex remains constant in the medium for a more prolonged period.

Another factor that Flox, C. *et al.* (2006) evaluated in their study was the addition of  $\text{Cu}^{2+}$  as co-catalyst, thus producing a higher amount of hydroxyl radicals ( $\cdot\text{OH}$ ) [63]. They experimented under the same experimental conditions as those abovementioned, but apart from adding a  $\text{Fe}^{2+}$  concentration of  $1 \text{ mM}$ , they also added  $0.25 \text{ mM}$  of  $\text{Cu}^{2+}$ . After 7 hours of reaction, they obtained a rapid degradation of all pollutants, including oxalic and oxamic acids, and a TOC removal of more than  $97\%$  [62] [63]. According to Flox, C. *et al.* (2006) and Enric Brillas (2014), this is due to the photolysis of Fe(III)-oxalate complexes and the high production of hydroxyl radicals from the  $\text{Cu}^{2+}/\text{Cu}^+$  catalytic system, among other things [62] [63].

Once the bibliographical review has been finished, it can be corroborated that there is not a large number of papers focusing on studying in-depth the abatement process of these two dyes, through the different Fenton processes at the desired experimental conditions. For this reason, considering the limited bibliography found and the fact that are promising techniques to treat textile effluents, it is proposed to deepen experimentally on the Photo-Fenton process, and examine the option of working at a neutral pH, thus making the process more applicable on an industrial scale.



## 5. MATERIALS AND METHODS

In this chapter, it is detailed all the different reagents and chemicals, the experimental devices and the diverse analytical methods used to carry out the experiments.

### 5.1. CHEMICALS AND REAGENTS

#### 5.1.1. Indigo carmine dye (IC)

The dye chosen for the different experiments is indigo carmine (IC), supplied by Panreac company. Below, there is a summary of the main characteristics of this dye (Table 15). Figure 9 shows the absorption spectrum of the indigo carmine dye, with its principal absorption bands. It can be concluded that the peaks of maximum absorbance of this dye are at 287 and 610 nm.

**Table 15.** Chemical properties of indigo carmine dye.

| <b>Indigo carmine dye</b>              |   |
|--|---|
| <b>IUPAC name</b>                      | disodium;2-(3-hydroxy-5-sulfonato-1H-indol-2-yl)-3-oxoindole-5-sulfonate                    |
| <b>Formula</b>                         | C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> S <sub>2</sub> |
| <b>CAS N°</b>                          | 860 - 22 - 0  |
| <b>C.I.</b>                            | 73015   |
| <b>Molecular weight</b>                | 466,36 g/mol  |
| <b>Purity</b>                          | > 95%   |
| <b>Synonyms</b>                        | Acid Blue 74, Indigotine, 5,5'-Indigosulphonic Acid Disodium Salt                           |
| <b>λ of max. ABS in H<sub>2</sub>O</b> | 606 - 612 nm  |

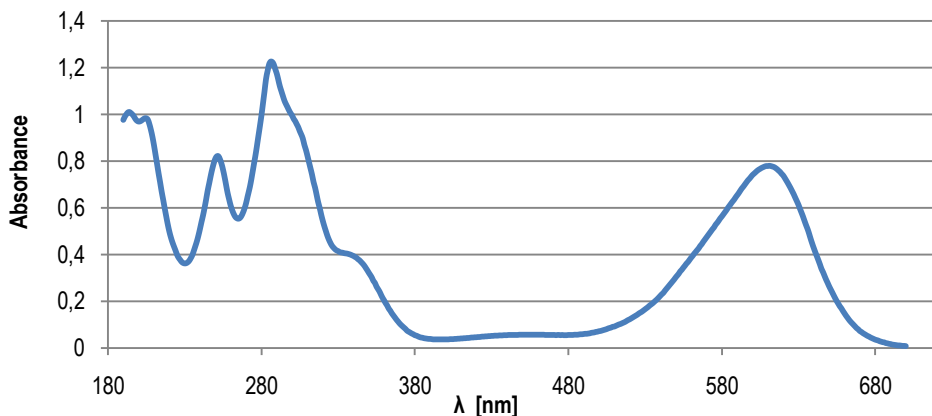


Figure 9. UV – VIS spectrum of indigo carmine dye.

### 5.1.2. Other reagents used

Table 16 shows the different reagents also employed, apart from the indigo carmine dye, in the experiments performed in this study. Besides, it is also included some information about these chemicals, such as CAS number or the company that supplied the reagent among others.

Table 16. Information about more reagents employed in the experiments.

| <u>Reagent</u>                            | <u>Formula</u>   | <u>CAS N°</u> | <u>Purity</u> | <u>Company</u>  |
|---|--|---------------|---------------|-----------------|
| Hydrogen peroxide                         | H <sub>2</sub> O <sub>2</sub>                                  | 7722 - 84 - 1 | 30% w/v       | Panreac         |
| Diethylenetriaminepentaacetic acid (DTPA) | C <sub>14</sub> H <sub>23</sub> N <sub>3</sub> O <sub>10</sub> | 67 - 43 - 6   | > 99%         | Sigma - Aldrich |
| L(+)-Ascorbic acid                        | C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>                   | 50 - 81 - 7   | > 99%         | Panreac         |
| 1,10 - Phenanthroline monohydrate         | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O               | 5144 - 89 - 8 | > 99%         | JT Baker        |
| Ammonium metavanadate                     | (NH <sub>4</sub> ) <sub>2</sub> V <sub>6</sub> O <sub>16</sub> | 7803 - 55 - 6 | > 99%         | Sigma - Aldrich |
| Acetic Acid                               | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>                   | 64 - 19 - 7   | > 99%         | Sigma - Aldrich |

## 5.2. ANALYTICAL METHODS

The different measurements and measuring devices used in this study are explained below.

### 5.2.1. Determination of the UV–VIS spectrum

The spectrophotometer HACH LANGE DR 6000 was used to perform the absorption spectrum of the indigo carmine dye (Figure 9). Besides, it was also used to check that there was no interference between the different substances present in the solution. The solution was transferred to a rectangular quartz cell and deposited in the spectrophotometer to obtain the corresponding absorption value for each wavelength.

### 5.2.2. Determination of indigo carmine concentration

The absorbance of the different samples of indigo carmine was obtained from the spectrophotometer HACH LANGE DR 3900, at a wavelength of 610 nm according to the UV-VIS spectrum of the indigo carmine dye (Figure 9). The samples analysed in the spectrophotometer were previously filtered through a 0.45  $\mu\text{m}$  nylon filter and driven into a 4 mL vial. Afterwards, they were analysed immediately, as it was decided not to stop the reaction.

Once the absorbance values were obtained from the different samples, taken from the reactor at different time intervals, the concentration of the indigo carmine was obtained through the calibration previously performed.

### 5.2.3. Determination of total iron concentration

The total iron concentration was determined according to ISO 6332:1998, which is based on a spectrometric method using 1,10 - phenanthroline and is applicable only for concentrations between 0.01 - 5 ppm [64]. This method consists of a mixture of 1 mL of acetic acid, 1 mL of 1,10 - phenanthroline and 4 mL of the sample extracted from the reactor. Besides, a small amount of ascorbic acid is also added to reduce the entire excess of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , thus obtaining the total concentration of iron.

This is a colorimetric method since initially the complex has a red-orange colour and is gradually discolouring over time. For this reason, it is expected approximately 24 hours to perform the measurement. This fact allows ensuring that all the iron has been reduced. Once the absorbance is measured in the HACH LANGE DR 3900 spectrophotometer at a wavelength of 510 nm, total iron concentration can be known through the calibration previously performed.

### 5.3. EXPERIMENTAL DEVICES

The different experimental devices used to carry out the experiments are explained in detail.

#### 5.3.1. BLB reactor

This reactor is a device equipped with up to 3 BLB lamps (Black light blue lamps), of 8 W of power each one. The lights emit radiation between 290 - 400 nm, with a maximum of approximately 365 nm. Besides, the reactor is connected to a thermostatic water bath, as shown in Figure 10. The water circulation allows surrounding the main tank with a jacket, controlling so that the temperature remains stable within a few values, to achieve optimal results. The reactor is situated above a magnetic stirrer to homogenize the solution.

Below, Table 17 shows the main characteristics of the BLB reactor, detailing the reactor volume, operating temperature or the total power emitted, among other aspects.

**Table 17.** Main features of the BLB reactor.

| <b>BLB reactor</b> |                         |
|--------------------|-------------------------|
| Volume             | 2 L                     |
| Number of lamps    | 1 - 3                   |
| Power              | 8 - 24 W                |
| ID                 | Philips TL 8 W – 08 FAM |
| Wavelength range   | 290 - 400 nm            |
| Maximum radiation  | 365 nm                  |
| Temperature        | 25 °C                   |
| Stirring system    | Magnetic                |



**Figure 10.** BLB reactor connected to a thermostatic water bath.

### 5.3.2. LED reactor

This reactor is equipped with a sheath containing a total of eight uniformly distributed LEDs (Light-emitting diode). The set of LEDs emits a total power of approximately 8 W, at a single wavelength of 365 nm. The experimental device also has a magnetic stirrer to homogenize the solution. Besides, the same as in the BLB reactor, there is a thermostatic water bath, which through water recirculation, allows forming a cooling jacket surrounding the main tank. Table 18 shows the main features of the reactor and the LED lamp used.

**Table 18.** Main features of the LED reactor.

| LED reactor     |          |
|-----------------|----------|
| Volume          | 2 L      |
| Number of LEDs  | 8        |
| Total power     | 8 W      |
| Wavelength      | 365 nm   |
| Temperature     | 25 °C    |
| Stirring system | Magnetic |

## 5.4. EXPERIMENTAL PROCEDURE

Firstly, a 50 ppm solution of indigo carmine is prepared in a volume of 2 L, so that it can be adjusted to the size of the experimental device. There is also added the quantity of chelating agent, needed to work with an iron concentration of 5 ppm. Even though the maximum value of iron permitted by law is 10 ppm, the main reason to operate with 5 ppm is an economical issue, since the reagent is not relatively cheap, and also to determine in this way the concentration of total iron present in the solution through the 1.10 – phenanthroline procedure.

Once everything is prepared, the solution is transferred into the reactor, also maintaining the stirring rate constant. The tank is sealed and adjusted with the lamps and then, the  $H_2O_2$  quantity needed to perform the experiments is added. Then just at that time, the abatement reaction starts.

The sample at time 0 is taken from the reactor before the  $H_2O_2$  amount is added. However, the other samples are taken approximately every 10 - 15 minutes of the reaction. The maximum quantity that can be extracted from the reactor to analyse is only 10% of the total volume. All samples are filtered by 0.45  $\mu m$  nylon filters to large vials, thus preventing undissolved iron from causing an erroneous reading. From these vials, it is taken the solution amount required to determine the concentration of indigo carmine and total iron, as explained above.

## 6. RESULTS AND DISCUSSION

Table 19 shows a summary of the different experimental conditions proposed for each of the experiments performed in this study and, the main results obtained.

**Table 19.** Summary of the main experimental conditions and results obtained from the different experiments performed.

| Exp. | Process      | pH            | Light Source | Fe <sup>2+</sup> [ppm] | H <sub>2</sub> O <sub>2</sub> [ppm] | IC [ppm] | Discolouration [%] | Time [min] |
|------|--------------|---------------|--------------|------------------------|-------------------------------------|----------|--------------------|------------|
| 1    | Photo-Fenton | Circumneutral | LED – 8 W    | 5                      | 200                                 | 50       | 99                 | 315        |
| 2    | Photo-Fenton | Circumneutral | BLB – 8 W    | 5                      | 200                                 | 50       | 99                 | 204        |
| 3    | Photo-Fenton | Circumneutral | BLB – 24 W   | 5                      | 200                                 | 50       | 98.1               | 100        |
| 4    | Photo-Fenton | Circumneutral | BLB – 24 W   | 5                      | 100                                 | 50       | 99                 | 120        |

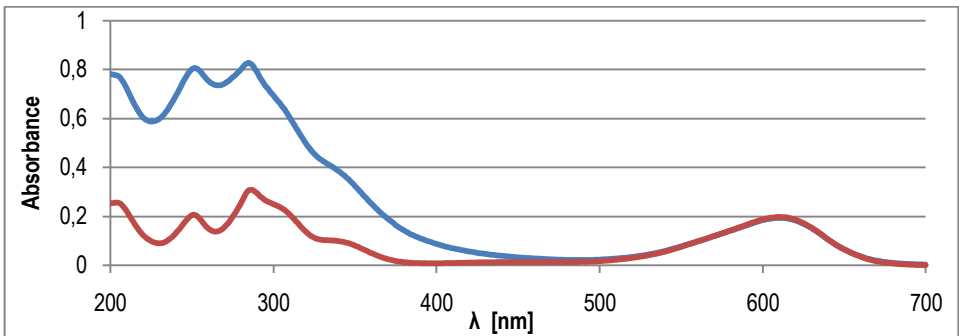
### 6.1. PHOTO-FENTON RESULTS AT CIRCUMNEUTRAL PH

#### 6.1.1. Chelating agent selection

As explained above, chelating agents allow to operate at a neutral pH and maintaining the soluble iron, thus avoiding the precipitation of inactive iron oxyhydroxides [43] [46]. The chelating agent chosen for the different experiments performed was the DTPA. The molecular formula and molecular weight of this compound, widely used in agriculture as micronutrient fertilizers, are C<sub>14</sub>H<sub>23</sub>N<sub>3</sub>O<sub>10</sub> and 393.35 g/mol, respectively. This chelating agent selection is because using this compound, the wastewater treated could be employed directly in agriculture,

without needing to separate [47]. Besides, the fact that no large variety of studies using DTPA, as the chelating agent in the Photo-Fenton process, has been found is also a significant reason to study its effects.

It is performed a spectral scanning within the UV-VIS range for both an indigo carmine solution and an indigo carmine solution with DTPA. It has been proved that in both cases, the absorption peak corresponding to the colour, located at 610 nm, is not altered (Figure 11). For this reason, it can be concluded that the use of DTPA as a chelating agent does not negatively affect the abatement of the solution and allow the monitoring of the IC through this technique.



**Figure 11.** UV – VIS spectrum: indigo carmine solution (■); indigo carmine + DTPA solution (■).

### 6.1.2. Comparison of different light source

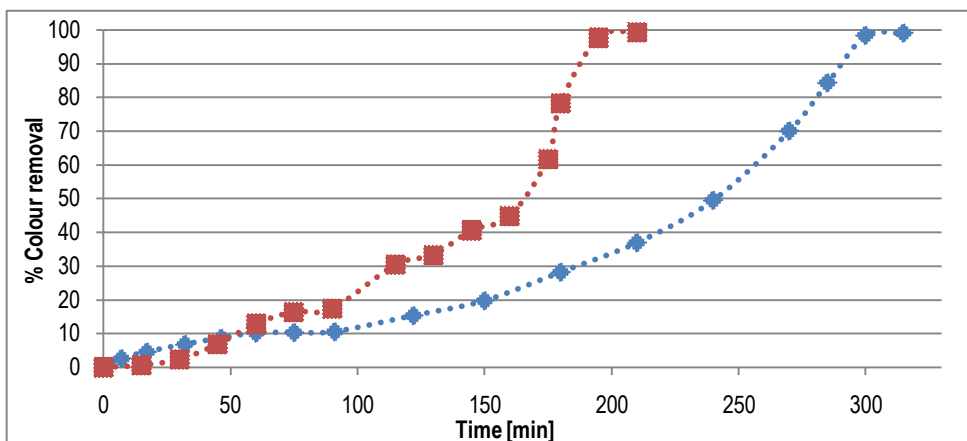
Operating at a circumneutral pH, with DTPA as a chelating agent, the type of light source used in the Photo-Fenton process may significantly affect the discolouring efficiency of the indigo carmine solution. It has been performed a comparison between two different light source types: the LEDs and the BLB lamp. The first one virtually works at a single wavelength, while the second one has a broad emission range, namely between 290-400 nm, despite having the maximum peak at 365 nm [65]. The spectrum difference and geometry are the main crucial factors that allow differentiation between the two experiments performed.

Both *Experiment 1* and *Experiment 2* were carried out under the same experimental conditions, with a  $\text{Fe}^{2+}$  concentration of 5 ppm within the DTPA, an initial concentration of  $\text{H}_2\text{O}_2$  of 200 ppm and an indigo carmine concentration of 50 ppm. Besides, the total power applied in both experiments was 8 W.



The results obtained both in *Experiment 1* and *Experiment 2* are shown in Figure 12. It is observed that almost complete discolouration is achieved in both cases. In particular, using BLB lamps allows a 99% colour reduction in a reaction time of 204 minutes, while the use of LEDs allows achieving the same percentage of discolouration, but in 315 minutes of reaction.

The time it takes to reduce the solution colour is the main drawback of both experiments. If it is compared them to each other, the time required with LEDs is considerably longer than the time needed with the BLB lamp. According to López-Vinent, N. *et al.* (2020), this may be associated with the radiation distribution within the reactor. The emission angle for the BLB lamp is 360°, whereas, for the set of LEDs is only 125°, which implies the formation of possible dark areas in the latter [65].



**Figure 12.** Comparison of different light sources in Photo-Fenton process at circumneutral pH, with DTPA as chelating agent. Experimental conditions:  $[\text{Fe}^{2+}] = 5$  ppm;  $[\text{H}_2\text{O}_2] = 200$  ppm;  $[\text{IC}] = 50$  ppm.

(■) BLB lamp; (◆) LEDs;

Concerning the total iron concentration present in the solution, it has been established that working with chelating agents, specifically with DTPA, has allowed the iron to remain practically soluble throughout the process, and thus preventing the precipitation of iron oxyhydroxides. At 15 minutes of reaction, in both experiments, the concentration of total iron was of 5 ppm. Later in the process, after 145 minutes, the total iron concentration for BLB – 8 W and LEDs – 8 W systems was 4.71 and 4.67 ppm, respectively.

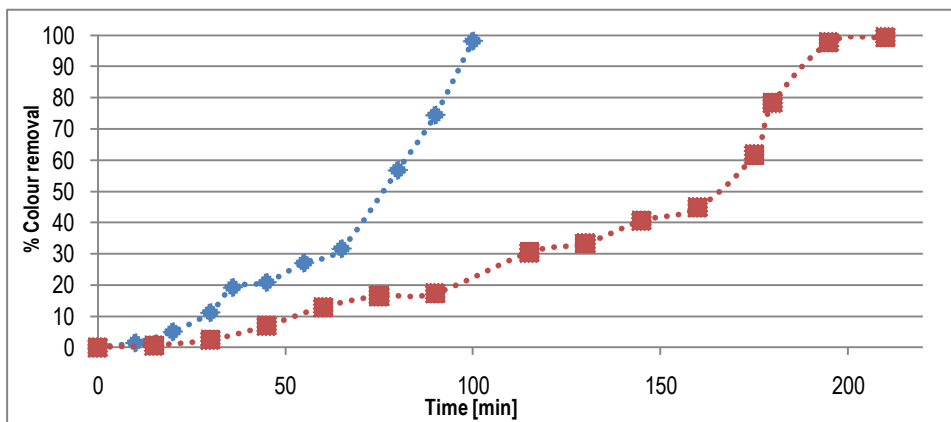
### 6.1.3. Comparison of different BLB lamp power

It has decided to study also the effect of the power of BLB lamps as a light source. To that end, it has proposed to perform two experiments at different values of power: 8 W and 24 W.

*Experiment 2* and *Experiment 3* have been carried out in the same reactor under the same experimental conditions: an initial  $\text{Fe}^{2+}$  concentration of 5 ppm included in the DTPA, a  $\text{H}_2\text{O}_2$  concentration of 200 ppm and an IC concentration of 50 ppm. A single BLB lamp was used to work at 8 W, while three BLB lamps were employed to work at a 24 W power.

As can be seen in Figure 13, in *Experiment 3*, a 98.1% discolouration of the IC solution has been achieved, in 100 minutes of reaction and using a power of 24 W. In contrast, for *Experiment 2*, working with 8 W of power, the discolouration obtained in 204 minutes was 99%.

It is true that by increasing the power from 8 W to 24 W, the complete discolouration can be achieved more quickly. This fact can be due to the generation of a higher amount of hydroxyl radicals, through the direct  $\text{H}_2\text{O}_2$  photolysis because of increasing the power [31].

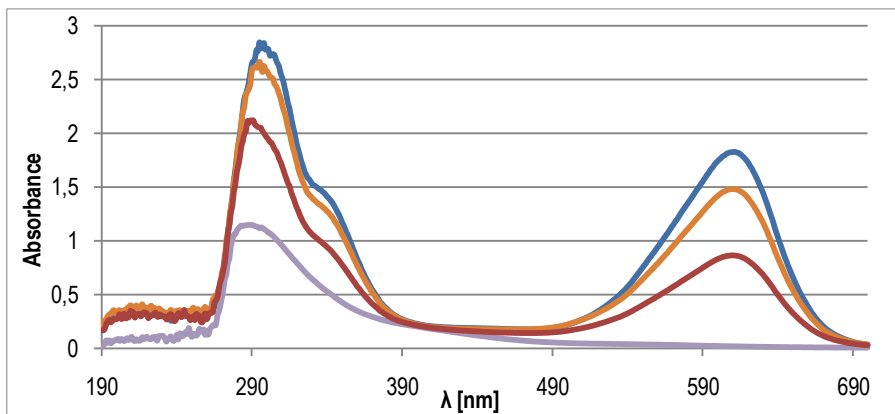


**Figure 13.** Comparison of different power of BLB lamps in Photo-Fenton process at circumneutral pH, with DTPA as chelating agent. Experimental conditions:  $[\text{Fe}^{2+}] = 5$  ppm;  $[\text{H}_2\text{O}_2] = 200$  ppm;  $[\text{IC}] = 50$  ppm.

(■) 24 W; (■) 8 W.

The initial reaction rate for the BLB system with 24 W power is  $9.416 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , while for the same operation but working with 8 W is  $2.854 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ . The ratio between both is approximately 3.3. One may conclude that increasing the power from 8 W to 24 W, that is to say, in a proportion from 1 to 3, allows increasing the reaction rate also in a similar ratio.

Besides, in *Experiment 3*, it was also performed a spectral scan at different times, namely at 10, 55, 80 and 100 minutes of reaction, to know the mechanism of breaking the structure of the indigo carmine dye (Figure 14). It was observed that the characteristic peak of the indigo carmine dye, located at 610 nm, was the first to disappear. This peak corresponds to the chromophore group, namely the double bond responsible for the colour [66]. Then it is followed by the break of the benzene ring, which corresponds to the maximum peak of 287 nm.



**Figure 14.** UV-VIS scanning of a 50 ppm IC solution at different times of the Photo-Fenton process at circumneutral pH. . (—) 10 min.; (—) 55 min.; (—) 80 min.; (—) 100 min.

#### 6.1.4. Comparison of different H<sub>2</sub>O<sub>2</sub> concentration

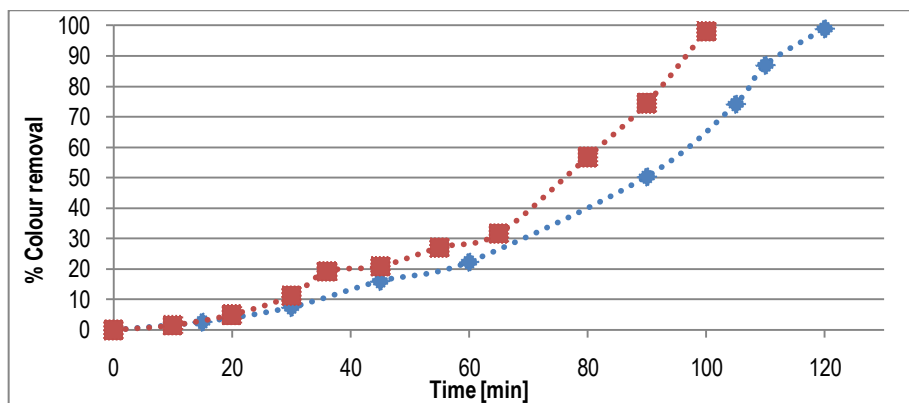
As explained above, the hydrogen peroxide concentration is one of the determining factors in the overall efficiency of the abatement process and, it should be adjusted so that the total amount of reagent used reacts completely and efficiently during the process [31]. It has been proposed to compare two different values of the initial concentration of hydrogen peroxide, and to observe their influence on the discolouration of an indigo carmine solution, using the Photo-Fenton process at circumneutral pH. The different amounts of H<sub>2</sub>O<sub>2</sub> proposed for comparison have been 100 and 200 ppm.

*Experiment 3* and *Experiment 4* were performed under the same experimental conditions, using the DTPA as a chelating agent with a Fe<sup>2+</sup> concentration of 5 ppm, and a concentration of

indigo carmine dye of 50 ppm. Both experiments were also carried out in a reactor with three BLB lamps and total power of 24 W.

As can be observed in Figure 15, in *Experiment 3*, using an initial  $\text{H}_2\text{O}_2$  concentration of 200 ppm, it is obtained a discolouration of 98.1%, in 100 minutes of reaction. On the other hand, in *Experiment 4*, a 99% of discolouration is achieved in 120 minutes of reaction, working with an initial  $\text{H}_2\text{O}_2$  concentration of 100 ppm.

It has been proved that by working at a higher initial concentration of hydrogen peroxide, keeping the  $\text{Fe}^{2+}$  application constant, there is also a small increase in the efficiency of the discolouring process. This process improvement by increasing the amount of oxidant can be due among other aspects to a higher production of hydroxyl radicals, and consequently, a higher rate of matter abatement. It is important to note that there is also a limit, from which the opposite effect takes place, that is to say, the percentage of abatement of the solution decreases due to the scavenging effect of the hydroxyl radicals.



**Figure 15.** Comparison of different concentrations of  $\text{H}_2\text{O}_2$  used in the Photo-Fenton process at circumneutral pH with DTPA as a chelating agent. Experimental conditions:  $[\text{Fe}^{2+}] = 5$  ppm;  $[\text{IC}] = 50$  ppm.

(■) 100 ppm of  $\text{H}_2\text{O}_2$  ; (■) 200 ppm of  $\text{H}_2\text{O}_2$ .

As can be seen, the curves of the different experiments have a slow initial stage and a later one faster. This strange shape of the curve can be due, among other aspects, to being at ratios of  $\text{IC}/\text{Fe}^{2+}$  and  $\text{IC}/\text{H}_2\text{O}_2$  far from the optimal. To confirm this point, further experiments at a lower indigo carmine concentration would have been necessary.

## 7. CONCLUSIONS

- In the different Fenton processes, it has been found that by operating with a higher amount of catalyst, within a determined range, it can be observed both an improvement on the abatement rate of the dyes and higher discolouration efficiency.
- In the different techniques, working with a lower concentration of dye, being indigo carmine or methyl orange, allows obtaining a higher dye's abatement in a shorter time. It has also found that an optimal operation ratio of dye/H<sub>2</sub>O<sub>2</sub> to use in the abatement process could be 1/108.
- It has been confirmed that the optimal pH value for the abatement process of indigo carmine and methyl orange dye, through the different Fenton techniques, is around 3.
- The overall efficiency of the different Fenton processes is directly determined, among other factors, by the initial concentration of H<sub>2</sub>O<sub>2</sub>. Working with a higher initial concentration of oxidant allows achieving a better abatement, up to a threshold value, from which the process efficiency is considerably reduced.
- In the Electro-Fenton process, the use of a BDD anode allows a higher reduction of TOC. Besides, working with this type of anode, at higher current densities, complete mineralization is achieved in shorter reaction time.
- The addition of a light source, like BLB lamps or LEDs, enables to generate a more elevated amount of hydroxyl radicals, but the geometry and the spectrum range of each one are key factors determining the abatement rate of the dyes, through the Photo-Fenton techniques.
- In the Photo-Electro-Fenton and other processes, it can be generated some stable recalcitrant intermediates, that are difficult to destroy and make it complicated to decrease the TOC.

- The use of DTPA, as a chelating agent, in the Photo-Fenton process at circumneutral pH for the abatement of indigo carmine dye, allows maintaining practically all iron soluble throughout all the experiment.
- Concerning the type of light source used, both BLB lamps and LEDs can produce a complete discolouration of the solution. To obtain a 99% discolouration, through the Photo-Fenton process at circumneutral pH, working with LEDs – 8 W requires 315 minutes of reaction, whereas the use of BLB set-up, at the same power, requires only 204 minutes.
- Working with a higher power with BLB lamps enables a better discolouration in a shorter time. In 100 minutes of reaction, operating with a 24 W power, it is achieved a 98.1%. Instead, in 204 minutes of reaction and 8 W of power, the solution is discoloured a 99%. Besides, by increasing power by a ratio from 1 to 3, the initial reaction rate also increases with a similar proportion.
- In the abatement process of an indigo carmine solution, through the Photo-Fenton process at circumneutral pH, using DTPA as a chelating agent, the double bond corresponding to the colour is first broken, followed by the break of the benzene ring.

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## ACRONYMS

|      |                                      |
|------|--------------------------------------|
| AOPs | Advanced Oxidation Processes         |
| BDD  | Boron-Doped Diamond                  |
| BLB  | Black Light Blue                     |
| BOD  | Biochemical Oxygen Demand            |
| C.I. | Colour Index                         |
| COD  | Chemical Oxygen Demand               |
| DTPA | Diethylenetriaminepentaacetic Acid   |
| EDDS | Ethylenediamine-N,N'-disuccinic Acid |
| EDTA | Ethylenediaminetetraacetic Acid      |
| EPs  | Emerging Pollutants                  |
| FP   | Plug Flow                            |
| IC   | Indigo carmine                       |
| LED  | Light – Emitting Diode               |
| MO   | Methyl Orange                        |
| Pt   | Platinum                             |
| Si   | Silicon                              |
| TOC  | Total Organic Carbon                 |
| UN   | United Nations                       |
| UV   | Ultraviolet                          |



# APPENDICES





## APPENDIX 1: CONCENTRATIONS AND DISCOLOURATION FOR EACH EXPERIMENT AT DIFFERENT TIMES

Photo-Fenton process at circumneutral pH with DTPA as chelating agent

*Experiment 1.* LEDs – 8 W as light source.

| Time [min] | % Colour removal | Concentration of total iron [ppm] |
|------------|------------------|-----------------------------------|
| 0          | 0                | 5                                 |
| 7          | 2,6818           | 5                                 |
| 17         | 4,6364           | 4.9                               |
| 32         | 6,9091           | 4.85                              |
| 46,3       | 8,7273           | 4.83                              |
| 60         | 10,2727          | 4.75                              |
| 75         | 10,4091          | 4.40                              |
| 90         | 10,6364          | 4.71                              |
| 122        | 15,4091          | 4.78                              |
| 145        | 19,8182          | 4.67                              |
| 180        | 28,2727          | 4.63                              |
| 210        | 37,0000          | 4.59                              |
| 240        | 49,5455          | 4.60                              |
| 270        | 70,0909          | 4.53                              |
| 285        | 84,3182          | 4.52                              |
| 300        | 98,3636          | -                                 |
| 315        | 99,0455          | -                                 |

**Experiment 2.** BLB – 8 W as light source.

| Time [min] | % Colour removal | Concentration of total iron [ppm] |
|------------|------------------|-----------------------------------|
| 0          | 0                | 5                                 |
| 15         | 0,6769           | 5                                 |
| 30         | 2,3917           | 4.96                              |
| 45         | 6,9043           | 4.96                              |
| 60         | 12,9061          | 4.95                              |
| 75         | 16,4711          | 4.86                              |
| 90         | 17,3736          | 4.92                              |
| 115        | 30,4152          | 4.87                              |
| 130        | 33,3484          | 4.75                              |
| 145        | 40,6137          | 4.71                              |
| 160        | 44,8105          | 4.17                              |
| 175        | 61,7780          | 4.64                              |
| 180        | 78,2942          | 4.60                              |
| 195        | 97,6986          | -                                 |
| 204        | 99,0072          | -                                 |
| 210        | 99,3682          | -                                 |

**Experiment 3.** BLB – 24 W of power and 200 ppm of H<sub>2</sub>O<sub>2</sub>.

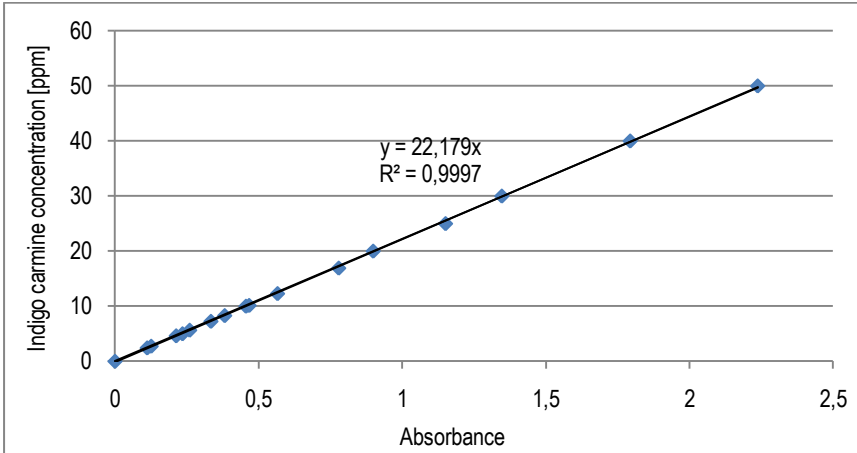
| Time [min] | % Colour removal |
|------------|------------------|
| 0          | 0                |
| 10         | 1,5335           |
| 20         | 5,0651           |
| 30         | 11,1989          |
| 36         | 19,2379          |
| 45         | 20,8643          |
| 55         | 27,0911          |
| 65         | 31,6450          |
| 80         | 56,7844          |
| 90         | 74,4424          |
| 100        | 98,1413          |

**Experiment 4.** BLB – 24 W of power and 100 ppm of H<sub>2</sub>O<sub>2</sub>.

| Time [min] | % Colour removal |
|------------|------------------|
| 0          | 0                |
| 15         | 2,6718           |
| 30         | 7,4905           |
| 45         | 16,0782          |
| 60         | 22,3760          |
| 90         | 50,3817          |
| 105        | 74,2366          |
| 110        | 87,0229          |
| 120        | 98,9981          |

## APPENDIX 2: CALIBRATION

### Indigo carmine calibration



### Calibration of total iron after adding ascorbic acid

