



Department of Civil Engineering and Computer Science Engineering

Bachelor thesis in Industrial Engineering degree

Advanced oxidation of methylene blue by a Fenton process

Student: Vicente Collado Torres

Tutor: Professor Renato Baciocchi

Co-Tutor: Professor Daniela Zingaretti

Giovanni Scaggiante

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Abstract

This bachelor experimental thesis was carried out in the Laboratory of Environmental Engineering of the University of Rome Tor Vergata and was focused on the decolorization of methylene blue (MB), a dye often used in the industrial textile sector, through the Fenton process and nanobubbles. The Fenton process is a known advanced oxidation method that involves the use of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) to generate highly reactive hydroxyl radicals ($\cdot\text{OH}$) that can quickly oxidize organic and inorganic compounds.[2] This process is widely used to treat different contaminants from dye wastewater; however, it is important to develop new technologies to increase the removal and sustainability of the process.

In this work, the application of air nanobubbles for the enhancement of the Fenton reaction was also evaluated. Nanobubbles are tiny bubbles which have a diameter of less than 100 nm, with special chemical characteristics that make them desirable for use in a variety of applications. [5] The positive effect of nanobubbles in the Fenton process is currently being investigated in the scientific literature because of the increase on mass transfer rates of the reactants, the increase of contact area between the reactants and pollutants, and the higher production of hydroxyl radicals [11].

The first section of the introduction to this thesis discusses the advanced oxidation processes, highlighting the main uses and the different options of processes. The second section explains with more details the Fenton process, focusing on the general characteristics and the variables that affect the process, also the nanobubbles are introduced. The final section explains the goals of the experimental activities.

The second chapter of this thesis explains the materials and methods used during the experimental sessions performed within this project, which are the techniques and procedures used to study the blue methylene decolorization using the Fenton reaction.

The third chapter shows the experimental results of the Fenton process for the decolorization of methylene blue with and without nanobubbles, comparing different operating conditions such as the MB/ H_2O_2 ratio, $\text{H}_2\text{O}_2/\text{Fe}$ ratio, or the pH.

Based on the preliminary results obtained in this work, it seems that the use of nanobubbles in the Fenton process for the removal of methylene blue, at least in the tested conditions, is not effective in enhancing the efficiency and sustainability of the process. However, the results didn't draw a clear conclusion about the hypothesis that the use of nanobubbles increased the efficiency of methylene blue degradation compared to the Fenton process without nanobubbles. Further research is needed to improve the nanobubble understanding by testing different experimental conditions and explore how this method might be used to remove other pollutants from wastewater.

1 Advanced Oxidation Processes (AOPs)

1.1 Introduction to Advanced Oxidation Processes

In our pursuit of developing advanced, environmentally friendly treatment technologies, the need to address environmental pollution and the challenges posed by industrialization has become increasingly apparent. This is where advanced oxidation processes (AOPs) come into play, offering efficient solutions for the treatment of various toxic organic pollutants and the complete destruction of emerging contaminants such as naturally occurring toxins, pesticides, and dyes [8].

AOPs encompass a range of oxidative water treatments used for the purification of toxic effluents in industrial settings, hospitals, and wastewater treatment plants. AOPs are a set of chemical treatment procedures designed to remove organic and sometimes inorganic materials in water and wastewater by oxidation through reactions with highly reactive species, such as hydroxyl radicals ($\cdot\text{OH}$), that can convert contaminants into smaller molecules or completely mineralize them. [14] AOPs encompass a broad range of methods, like the utilization of strong oxidizing agents such as hydrogen peroxide (H_2O_2) or ozone (O_3), catalysts such as iron ions, electrodes, or metal oxides, and irradiation sources including UV light, solar light, or ultrasounds [8]. The main difference between AOPs and classic oxidation reactions lies in the mechanism and the reactants involved. AOPs rely on the generation of radicals to initiate the oxidation process, while classic oxidation reactions involve direct electron transfer between reactants. [14] Over time, several studies have reviewed different AOPs employed for the degradation of recalcitrant compounds, providing valuable insights into their efficacy and applicability. Notable examples of AOPs include Fenton, photo-Fenton, UV/ H_2O_2 , UV/ O_3 , nonthermal plasmas, sonolysis, photocatalysis, radiolysis, and supercritical water oxidation processes [8].

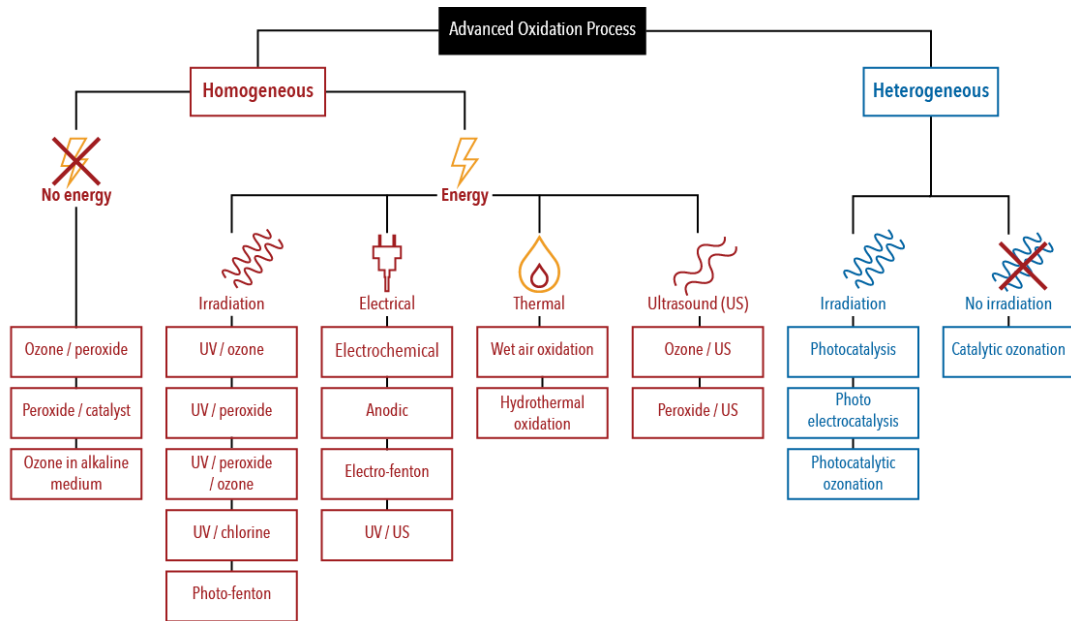


Figure 1. Main Advanced oxidation processes (www.globalwaterintel.com)

Hydroxyl radicals, known for their efficiency and effectiveness, play a crucial role in AOPs by interacting with organic pollutants through addition or hydrogen abstraction pathways. The oxidation products are often less toxic and more amenable to bioremediation, such as CO₂ and water. The overall efficiency of AOPs depends on factors such as the chosen AOP method, the physical and chemical properties of the target pollutant, and the operating conditions employed [8].

Even if the installation costs of AOPs are relatively low, the operating costs can be high due to the input of chemicals and energy required. To mitigate these costs, AOPs are often employed as a pre-treatment combined with biological treatment methods. The combination of various AOPs has proven to be a highly effective approach for enhancing pollutant removal while simultaneously reducing costs. While AOPs are not commonly utilized for disinfection purposes due to the short half-life of hydroxyl radicals, AOPs can serve as a polishing step to eliminate micro-pollutants from wastewater and facilitate water disinfection [8].

One of the primary advantages of AOPs over other treatment processes lies in their ability to degrade compounds present in wastewater rather than concentrating or transferring them into a diffused phase. This prevents the generation and disposal of

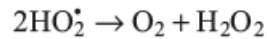
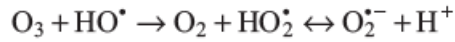
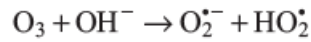
secondary waste materials, making AOPs a superior choice in terms of sustainability and waste management. [8]

1.2 Different Options of Advanced Oxidation Processes.

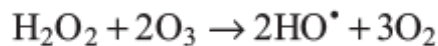
1.2.1 Ozonation at High pH and Ozonation in the Presence of H₂O₂

Ozone (O₃) has emerged as a prominent tool for the oxidation of organic pollutants, employing two distinct types of oxidation reactions:

- The first involves direct reactions with molecular ozone, known as ozonolysis. Molecular O₃ reactions exhibit exceptional selectivity, primarily targeting unsaturated aromatic and aliphatic compounds. The range of molecular O₃ reactions is diverse, encompassing processes such as oxygen atom transfer to anionic, uncharged, and cationic species, electron transfer, formation of oxyl radicals, O₃ molecule addition, and ring formation.
- The second entails indirect oxidation through the participation of free radicals generated during ozone decomposition, that is influenced by various factors, including pH and the presence of inorganic and organic compounds [7]. Under alkaline conditions with the presence of hydroxyl ions (HO⁻), O₃ decomposes in water, giving rise to highly reactive hydroxyl radicals (HO·). These HO· radicals possess a significantly higher oxidation potential (+2.8 V) compared to molecular O₃ (+2.07 V), enabling them to indiscriminately attack both organic and inorganic molecules at diffusion-limited reaction rates. [7] O₃ decomposition follows the following chain of reactions:



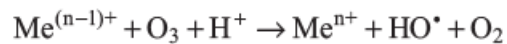
In a manner analogous to O_3 , hydrogen peroxide (H_2O_2) demonstrates both direct and indirect pathways for the oxidation of organic pollutants in water. Indirect reactions occur due to the oxidizing action of free radicals formed during photolytic or catalytically induced H_2O_2 decomposition. Despite H_2O_2 's substantial oxidizing capability, allowing for the oxidation of aldehydes, alcohols, amines, azobenzene, phenols, cyanides, reduced sulphur compounds, and metal ions, it alone cannot achieve complete mineralization of recalcitrant organic compounds or effectively remove toxicity. Although in the “peroxone” process ($\text{O}_3/\text{H}_2\text{O}_2$) HO^\bullet radicals generated by the reaction between O_3 and H_2O_2 , this treatment method has demonstrated to have a high degree of mineralization. [7] The “peroxone” process overall reaction is described below:



1.2.2 Catalytic Ozonation

Catalytic ozonation has emerged as a promising alternative for the degradation of organic compounds in recent years, introducing the utilization of transition metals as catalysts in the ozonation process. The investigation of catalytic ozonation can be categorized into two main types: homogeneous and heterogeneous processes.

- In homogeneous catalytic ozonation, transition metal ions, including Fe (II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(II), Cr(III), and Zn(II), are employed in conjunction with bulk O₃. These transition metal ions, when present in the reaction solution, initiate the decomposition of O₃ by generating superoxide radicals (O₂^{·-}). The transfer of one electron from the O₂^{·-} molecule to O₃ leads to the formation of ozonide (O₃^{·-}) and subsequently hydroxyl radicals (HO[·]). [7] A general homogeneous catalytic ozonation reaction between a metal Me⁽ⁿ⁻¹⁾⁺ and O₃ can be summarized as:



- Heterogeneous catalytic ozonation involves the utilization of metal oxides and metals, including noble metals supported on metal oxides, such as TiO₂, Al₂O₃, SiO₂, MnO₂, Fe₂O₃, Cu, Ru, Pt, Pb, Pd, Co, among others. These catalysts play a crucial role in facilitating the decomposition of O₃ and enhancing the generation of hydroxyl radicals (HO[·]). The effectiveness of heterogeneous catalytic ozonation is heavily dependent on the specific catalyst employed, its surface properties, and the solution pH. [7]

The selection and characterization of appropriate catalysts play a crucial role in determining the efficiency of catalytic ozonation. The choice of transition metal ions or metal oxides as catalysts, their surface properties, and the surrounding solution pH significantly influence the process's overall performance. By exploring the mechanisms and factors governing both homogeneous and heterogeneous catalytic ozonation, a deeper understanding can be attained regarding their potential applications in the degradation of organic pollutants. These catalytic ozonation processes provide an innovative approach towards efficient and environmentally friendly water treatment solutions. [7]

1.2.3 Fenton Process

The Fenton process is an advanced treatment process used for the removal of hazardous organic pollutants from refractory/toxic wastewater [12]. The process is based on the Fenton reaction, which involves the use of hydrogen peroxide and

ferrous ions to produce hydroxyl radicals that can oxidize organic pollutants [1] The Fenton reaction is given below:



Overall, the Fenton process is an effective treatment process for wastewater, but it has some limitations that need to be addressed. The optimization of the Fenton process can help to overcome these limitations and improve its efficiency.

The next chapter will delve further into the Fenton process.

1.2.4 Persulfate Oxidation

Persulfate oxidation offers an effective option for environmental remediation. There are many different persulfate salts; one of the most common in the environmental field is sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$). Persulfate salts exhibit dissociation in aqueous solutions, giving rise to the formation of the persulfate anion ($\text{S}_2\text{O}_8^{2-}$). This anion possesses formidable oxidizing capabilities, enabling the degradation of a wide array of environmental contaminants. Alternatively, persulfate can undergo catalysis with diverse reactants, leading to the generation of the sulphate radical ($\cdot\text{SO}_4$), an even more powerful oxidant. That process is also known as “activation”. The activation of $\text{S}_2\text{O}_8^{2-}$ to $\cdot\text{SO}_4$ can be achieved through several mechanisms, including elevated temperatures (35 to 40 °C), utilization of ferrous iron (Fe (II)), photo (UV) activation, alkaline conditions (elevated pH), or hydrogen peroxide (H_2O_2). The utilization of $\cdot\text{SO}_4$ in persulfate oxidation brings forward a greater oxidation potential (2.6 V) compared to $\text{S}_2\text{O}_8^{2-}$ (2.1 V), enabling the degradation of a bigger range of environmental contaminants at accelerated rates. [6]

1.3 Main Applications and Uses of Chemical Oxidation

1.3.1 Textile Wastewater Treatment

The treatment of textile industry wastewater poses significant challenges due to the extreme complexity and variability of dyehouse effluent samples. Evaluating and unifying treatability studies across the global textile industry becomes a perplexing task [7]. The main contaminants found in textile wastewater consist of chemical and biochemical parameters such as BOD₅, COD, NH₄-N, TSS, Fe, Cr, S²⁻, oil and grease. [7]

Dyes are aromatic organic compounds that possess light-absorbing properties and provide color to the visible region, have become integral to numerous industries worldwide. The extensive range of commercial dyes, exceeding 100,000 in number, contributes to an annual production estimated at approximately 1×10^9 kg. These dyes are employed to impart permanent color to various substrates, granting them resistance against fading caused by exposure to water, light, oxidizing agents, sweat, and microbial attack. [10]

The multitude of advantages offered by dyes has led to their extensive usage across diverse industries such as textiles, food, rubber, printing, cosmetics, medicine, plastic, concrete, and paper, serving a myriad of purposes. However, these industries collectively generate vast quantities of wastewater laden with toxic and carcinogenic dyes, rendering the water unfit for human consumption. Among the dye-consuming industries, the textile industry stands out as a prominent consumer, relying heavily on textile dyes characterized by their complex chemical structures. [7]

The removal of color, a crucial parameter in dyehouse effluent, is a primary concern due to its ecotoxicological risks and aesthetic considerations. Chemical oxidation processes effectively mitigate color, making them technically and economically feasible for color removal [7]. On the other hand, achieving complete oxidation within technically and economically viable treatment conditions is challenging. In fact, the abatement of chemical oxygen demand (COD) and total organic carbon (TOC) in textile wastewater is often incomplete. Therefore, a combination of advanced treatment processes, which are more energy-intensive and costly, should be considered alongside conventional methods for pre- or post-treatment purposes [7].

The choice of AOPs influences the formation of recalcitrant or toxic oxidation intermediates or end products during textile wastewater treatment. Considering that chemical oxidation aims to reduce toxicity and recalcitrance, preliminary treatability experiments are essential to identify potentially toxic oxidation intermediates under various chemical reaction conditions [7].

1.3.2 Pharmaceutical Wastewater Treatment

The presence and impact of pharmaceuticals in the environment, particularly in aquatic ecosystems, have garnered significant scientific attention. Despite their relatively low concentrations, ranging from ng/L to µg/L levels, pharmaceuticals can exert profound negative effects on the environment. The pharmaceutical industry utilizes various raw materials and generates a wide range of wastes and emissions, characterized by variability and complexity [7]. The main contaminants in pharmaceutical wastewater come from the solvents, catalysts and reactants that are used in the specific process, but also from wet scrubber and equipment cleaning operations. These wastewaters usually end in a high BOD, COD and TSS effluent at a pH ranging between 1 to 11. [7]

During the design of bulk manufacturing processes, careful consideration is given to the toxicity of starting materials, as well as the management of wastes such as stock solutions, filter residues, by-products, cleaning and rinse water, and emissions. Specific chemicals originating from pharmaceutical manufacturing processes primarily enter aquatic and terrestrial environments through various pathways, including industrial, agricultural, and domestic wastewater discharges. In some cases, these chemicals are not only refractory but also significantly inhibit conventional biological treatment processes. [7]

The scientific literature extensively covers the treatability of different drugs in aqueous solutions and/or model pharmaceutical wastewater, with a particular focus on chemical oxidation processes targeting typical pollutants in the pharmaceutical industry, such as analgesics, antibiotics, and hormones. However, drawing general conclusions about the applicability of chemical oxidation processes for actual

pharmaceutical wastewater treatment proves challenging due to the scarcity of comprehensive data on this specific subject. [7]

1.3.3 Chemical Industry Wastewater Treatment

The organic chemicals industry encompasses a diverse range of products, resulting in the generation of wastewaters with varying compositions. However, a common characteristic of these wastewaters is the presence of organic matter, a significant portion of which is biodegradable. Consequently, biological treatment processes play a pivotal role in mitigating water pollution, with all waste streams typically directed to biological treatment following suitable pre-treatment. While certain pollutants, such as heavy metals and cyanide, can be readily addressed at the source, the treatment of toxic organics is a formidable challenge, often needing complex treatment applications such as AOPs. [7] The main polluting parameters are organic matter expressed as COD, TOC, BOD₅, and VOC; oil and grease; SS; and pH. Nitrogen, phosphorus, cyanide, heavy metals, chloride, bromide, and sulphate could be also present in the wastewaters. [7]

The evaluation of chemical oxidation processes reveals not only existing and applied methods but also a plethora of new, highly efficient, and promising applications. Wet oxidation stands out as a versatile approach suitable for diverse waste components, demonstrating significant effectiveness in the destruction or conversion of chemicals into biodegradable forms. Electrochemical methods exhibit immense potential for both reduction and oxidation processes, with reductive dechlorination expected to play a crucial role in controlling chlorinated organic compounds. Other oxidation methods, notably Fenton's oxidation in combination with other oxidation agents, have proven highly effective against a broad spectrum of organic compounds. [7]

1.3.4 Metal Finishing Industry Wastewater Treatment

The metal finishing industry, one of the largest industrial sectors worldwide, extensively employs a wide array of chemicals in its operations. If not managed properly, these chemicals can pose significant risks to public health and the environment [7]. The main contaminants found in the metal finishing industry

wastewater are metals, cyanide, organic wastes, total suspended solids, and other inorganic pollutants such as sulphate, chloride, phosphates, fluoride and ammonia. [7]

Oxidation/reduction techniques employed in treating cyanide, hexavalent chromium, and precious metal-bearing wastewaters are well-established and straightforward. Notably, alkaline chlorination for cyanide destruction, chemical reduction using reduced sulphur compounds to reduce hexavalent chromium, and electrolytic metal recovery for precious metals represent the most common treatment methods in metal finishing industry facilities due to their moderate cost-effectiveness. When correctly applied, these methods can achieve satisfactory removal efficiencies that meet discharge standards. [7]

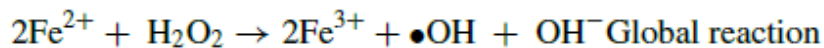
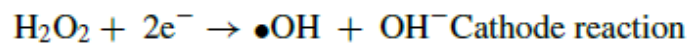
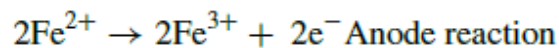
However, certain oxidation/reduction techniques, particularly those employed in treating complexed metals, exhibit sensitivity to reaction conditions. Misapplications of these methods may result in unsatisfactory pollutant removal efficiencies or partial oxidation, leading to the formation of by-products such as cyanate, ammonia, nitrate, and sulphate, which necessitate additional treatment steps prior to discharge into receiving environments. Hence, optimizing operational conditions becomes a crucial step to minimize sludge production, operating costs, and maximize process performance. [7]

Also, some AOPs are becoming a more common application on the metal finishing wastewater treatment, the most common of are ozonation, Fenton process and electrochemical oxidation, these prove a great potential but they present some issues such as the failure on the treatment of complexed metal cyanides such as iron and cobalt cyanides, the high operation costs on industrial scale applications or the formation of nitrate which may require of another process in order to complete the treatment. [7]

1.4 Fenton process

1.4.1 General Characteristics

The Fenton mechanism involves the reaction between ferrous ions and hydrogen peroxide, with ferrous ions acting as a catalyst for the decomposition under acidic conditions of H_2O_2 into a hydroxyl radical and hydroxyl anion. In this process, Fe^{2+} ions act as an anode by providing electrons, while H_2O_2 acts as a cathode, consuming electrons [2]. The spontaneity of this redox reaction is evidenced by the electromotive force of the redox system involved, where Fe^{2+} ($E = 0.77 \text{ V}$) acts as the anode and H_2O_2 ($E = 1.77 \text{ V}$) acts as the cathode, resulting in a final global reaction value of $E = +1.0 \text{ V}$. [2]. The process described before is summarized in the following reactions:



The success of the Fenton process can be attributed to its operational simplicity, ease of implementation, and flexibility for industrial applications, coupled with its high efficiency in pollutant mineralization. In comparison to other AOPs, the traditional Fenton process offers several advantages: it does not require energy for activating the chemical reaction to form hydroxyl radicals (energy is only needed for effluent pumping); the reaction occurs at room temperature and atmospheric pressure; relatively short reaction times are achieved; and the operation is simple, flexible, and easily adaptable for industrial-scale implementation. [2]

The Fenton process presents significant potential for wastewater treatment. Its utilization in the degradation of non-biodegradable organic compounds has proven effective, leading to the mineralization of pollutants and the generation of water, carbon dioxide, and inorganic ions as end products. The characteristics of the Fenton process, such as its

simplicity, versatility, and operational efficiency, contribute to its prominence as a viable solution for the remediation of recalcitrant compounds in industrial effluents. [2]

1.4.2 Variables Affecting the Fenton Process

The efficiency of the Fenton process is influenced by several key variables that must be carefully considered and optimized. These variables include pH, concentrations of hydrogen peroxide (H_2O_2) and reduced iron, as well as the use of promoting agents. Understanding and controlling these parameters are essential for maximizing the effectiveness of the Fenton process in wastewater treatment. [2]

pH plays a crucial role in the Fenton process, and maintaining the appropriate pH range is vital for optimal performance. The recommended pH range for the process is typically between 2.5 and 3.5. If the pH drops below 2.5, an excess of protons (H^+) in the reaction medium can consume hydroxyl radicals, negatively impacting the process. On the other hand, at pH levels above 4.0, ferrous ions tend to hydrolyze water, leading to the precipitation of ferric hydroxide ($\text{Fe}(\text{OH})_3$) and reducing the efficiency of the process. Therefore, controlling pH within the recommended range is essential to ensure effective hydroxyl radical generation and pollutant degradation. [2]

When adjusting pH, it is important to consider the characteristics of the acid used. Nitric acid (HNO_3), with its oxidizing character, can interfere negatively in the Fenton process by oxidizing ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}), which are inactive for the catalytic decomposition of H_2O_2 . Hydrochloric acid (HCl), although it has a reducing character, can also negatively interfere if it oxidizes to chlorine gas in the presence of strong oxidizing agents. In this context, sulfuric acid (H_2SO_4) is often the most recommended acid for pH adjustment due to its dehydrating characteristics and limited oxidative action at typical process temperatures. [2]

The concentration of ferrous ions used as catalysts in the Fenton process is another critical variable. While ferrous ions play a crucial role in the generation of hydroxyl radicals, an excess of these ions can have a negative effect by consuming the hydroxyl radicals themselves. Therefore, determining the optimal concentration of ferrous ions through experimental optimization is crucial for achieving efficient pollutant degradation. [2]

The concentration of hydrogen peroxide, the precursor of hydroxyl radicals, also requires careful optimization. Excessive concentrations of hydrogen peroxide can act as scavengers, eliminating hydroxyl radicals from the reaction environment and diminishing the degradation efficiency of organic pollutants. Therefore, experimental optimization is necessary to determine the optimal concentration of hydrogen peroxide to achieve effective hydroxyl radical generation and pollutant removal. [2]

In addition to pH, ferrous ion concentration, and hydrogen peroxide concentration, several other factors can influence the Fenton process. The type of effluent being treated, the concentrations of organic contaminants and inorganic salts, reaction time, and the choice of iron catalyst in heterogeneous systems are all important considerations. The presence of promoting agents such as short-chain carboxylic acids and phenolic compounds can also have a positive effect on the degradation speed and efficiency of the process. [2]

The promoting effect of carboxylic acids, demonstrated in previous studies, highlights their ability to enhance the Fenton process. Experimental evidence has shown that the addition of formic acid at an appropriate concentration can significantly improve color removal from the medium, emphasizing the importance of peracid formation and the higher energy associated with the resulting hydroxyl radical. Similar effects have been observed for other compounds, such as phenols, which can reduce iron (III) ions to the more active iron (II) species, thus enhancing the Fenton reaction. [2]

Moreover, other factors such as the type of effluent, the concentration of contaminants, the generation of by-products, and the temperature should be taken into account due to their influence on the Fenton process. The hydroxyl radical's non-selective nature can lead to the production of other compounds during the degradation process, requiring careful monitoring and management [2].

1.4.3 Fenton reaction enhancement by nanobubbles

Nanobubbles have recently emerged in the realm of wastewater treatment. These minute bubbles are generated from a gas infused with ozone or various gases under specific pressure and flow rate conditions. The extraordinary feature of this technique lies in its

ability to produce nanobubbles with diameters of less than 1 μm , allowing them to linger within the water column for extended durations compared to conventional bubbles, which rapidly ascend to the water surface and dissipate. [11] Due to their size, nanobubbles exhibit unique properties that improve numerous physical, chemical, and biological processes. They remain suspended in liquid and are stable due to their equilibrium with bubble surface tension, internal pressure, external pressure, surface charge, and their environment [13]

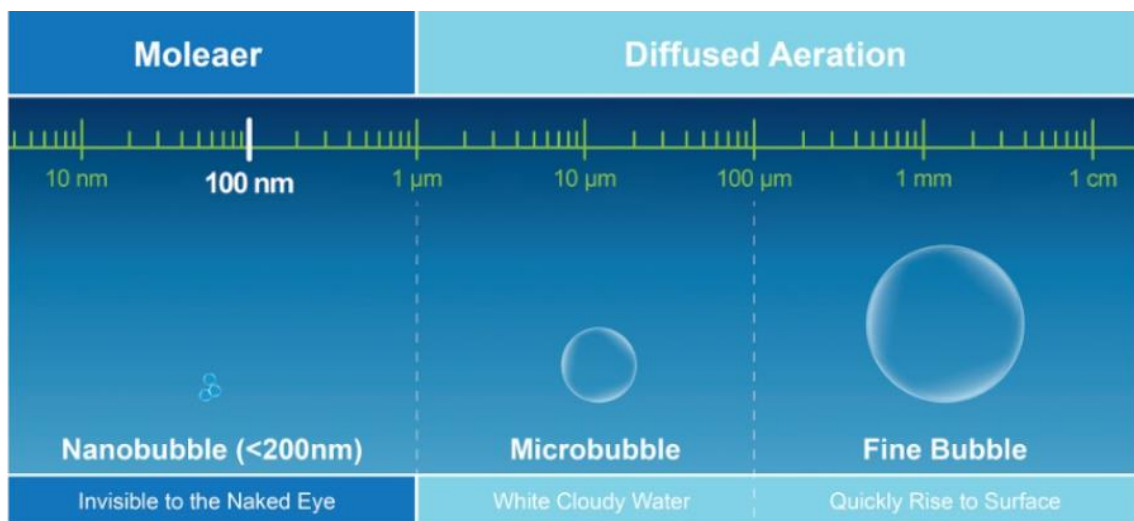


Figure 2. Comparison between different types of bubbles (<https://www.moleaer.com/nanobubbles>)

Fundamentally, nanobubbles create a diffusion barrier when a layer of contaminants adheres to their surfaces, resulting in the generation of hydroxyl free radicals ($\bullet\text{OH}$) upon bursting. This phenomenon, as previously mentioned, plays a pivotal role in the degradation of organic compounds present in wastewater, thereby highlighting the significance of nanobubbles in the pursuit of effective water treatment. [11]

The generation of nanobubbles encompasses three primary categories of generators: gas with flowing liquid, gas without liquid flow, and low-power generators. It is important to note that these categories do not represent an exhaustive list, as the generation of micro-nanobubbles can transcend these classifications. [11]

In wastewater treatment, the concept of nanobubble technology aligns closely with Advanced Oxidation Processes (AOPs), wherein the dissolution of air, oxygen, and ozone microbubbles within water gives rise to hydroxyl free radicals ($\bullet\text{OH}$) [11]. However, what

distinguishes nanobubble technology from AOPs is the mechanism by which $\bullet\text{OH}$ is formed. Unlike AOPs that rely on chemical additives, nanobubble technology achieves $\bullet\text{OH}$ generation through air bubbling, classifying it as a form of physical treatment rather than chemical treatment. Conversely, ozonation in AOPs rapidly decomposes in water, rendering it unstable over prolonged periods, whereas nanobubbles produced using ozone gas can persist within the water column for an extended duration. [11]

To enhance treatment efficiency, researchers have explored the combination of nanobubble technology with peroxide, such as H_2O_2 [11]. This hybrid approach yields stronger oxidizing agents, including peroxide ($\bullet\text{O}_2$) and superoxide ($\bullet\text{O}_2\text{H}$), which effectively accelerate the decomposition of pollutants. These stronger oxidants prove more adept at degrading pollutants, thus amplifying the remedial efficacy of the treatment process. [11]

As of now, the combination of nanobubble technology with other AOPs still needs to be explored, particularly concerning the removal of organic pollutants. For this, the potential application of this integrated approach in large-scale treatment needs to be more investigated [11].

2 Methylene blue (MB)

2.1 General properties

Methylene blue (MB) emerges as one of the most extensively utilized chemicals in the dye industry, finding applications in the coloring of silk, wool, cotton, and paper. [10]

MB, classified as an aromatic heterocyclic basic dye, possesses a molecular weight of 319.85 g/mol. With a molecular formula of $C_{16}H_{18}N_3C_1S$ and a maximum absorbance (λ_{max}) at 663 nm, MB stands as a well-known cationic and primary thiazine dye. Its high-water solubility enables the formation of a stable solution with water at room temperature. MB falls under the category of polymethine dyes, featuring an amino autochrome unit and carrying a positive charge. [10]

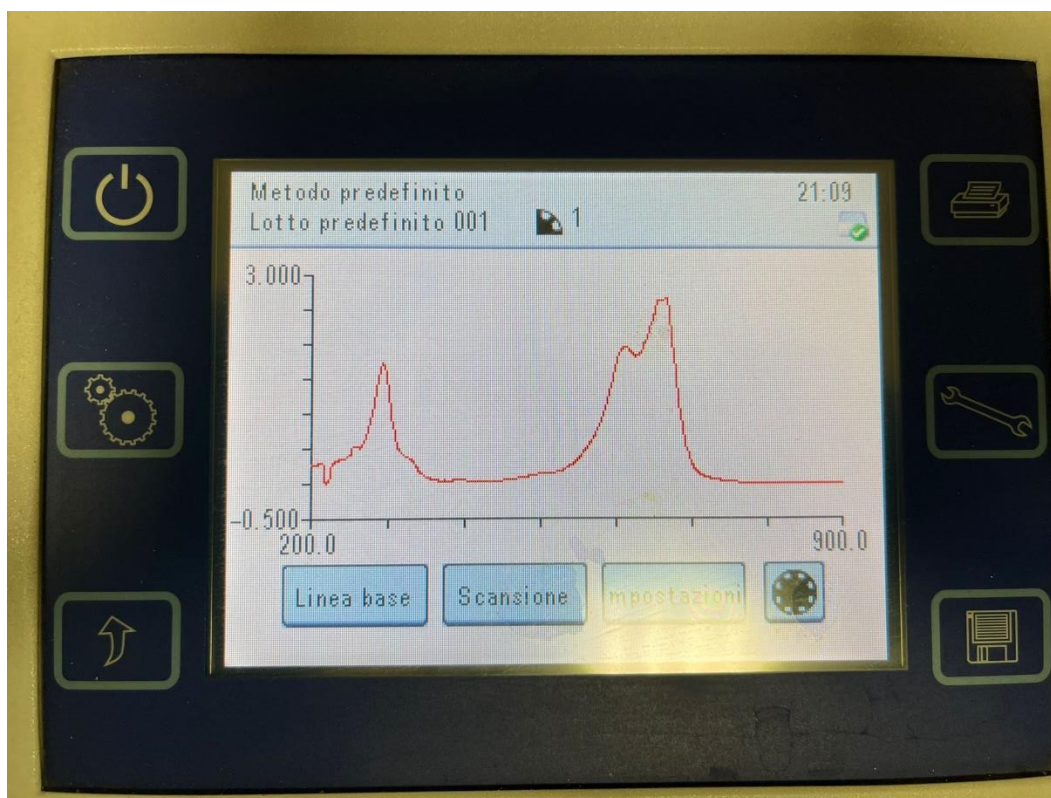


Figure 3. Methylene blue absorbance spectrum

2.2 Toxicological properties

The release of substantial amounts of methylene blue (MB) dyes from textile industries into natural water sources poses a significant health threat to both humans and microbial

life. This particular dye exhibits substantial toxicity, which raises concerns about its potential harmful effects on human health. MB is known to be toxic, carcinogenic, and non-biodegradable, posing grave risks to both human well-being and environmental stability. [10]

Exposure to MB can lead to a range of health risks for individuals, including respiratory distress, abdominal disorders, blindness, and digestive and mental disorders [10]. Its toxic properties can manifest in symptoms such as nausea, diarrhoea, vomiting, cyanosis, shock, gastritis, jaundice, methemoglobinemia, tissue necrosis, and increased heart rate. Moreover, MB can cause the premature death of cells in tissues and skin, along with skin and eye irritations, also, direct contact with MB may result in skin redness and itching. [10]

The discharge of MB into the environment poses a significant threat from both an aesthetic and toxicological standpoint. The presence of MB not only reduces light penetration but also generates highly colored by-products, even at low concentrations. This reduction in sunlight transmittance, attributed to MB's high molar absorption coefficient, diminishes oxygen solubility and interferes with the photosynthetic activity of aquatic life. [10]

3 Materials and Methods

For this chapter the different material and methods used in the experimental activities carried out in the laboratory of Environmental Engineering of the University of Rome Tor Vergata are described. In specific, different conditions were tested to evaluate the effectiveness of the decolorization on methylene blue with the Fenton process. Among them, also the use of nanobubbles within the Fenton process was assessed.

3.1 Reagents employed for the experimental tests

Methylene blue hydrate ($C_{16}H_{18}ClN_3S \cdot xH_2O$, $\geq 97.0\%$) was purchased from Fluka Analytical.



Figure 4. Methylene blue hydrate from Fluka Analytical

Iron(II) sulfate heptahydrate ($FeO_4S \cdot 7H_2O$, $\geq 99.0\%$) was purchased from Alfa Aesar.

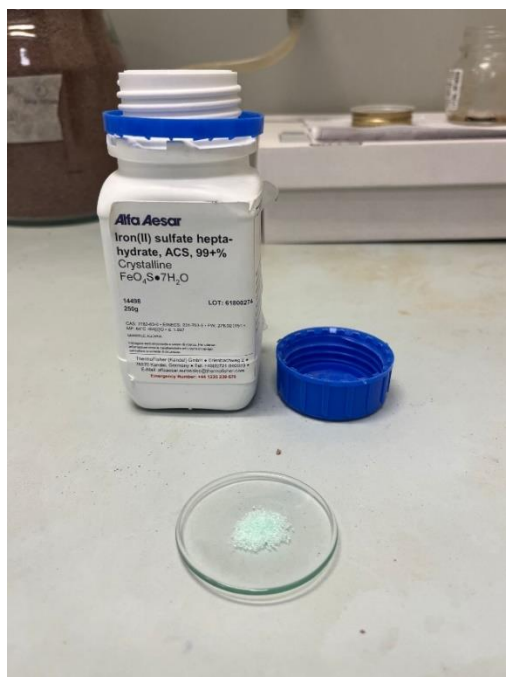


Figure 5. Iron(II) sulfate heptahydrate from Alfa Aesar.

Hydrogen Peroxide Solution (H₂O₂, ≥30%) was purchased from Sigma-Aldrich.

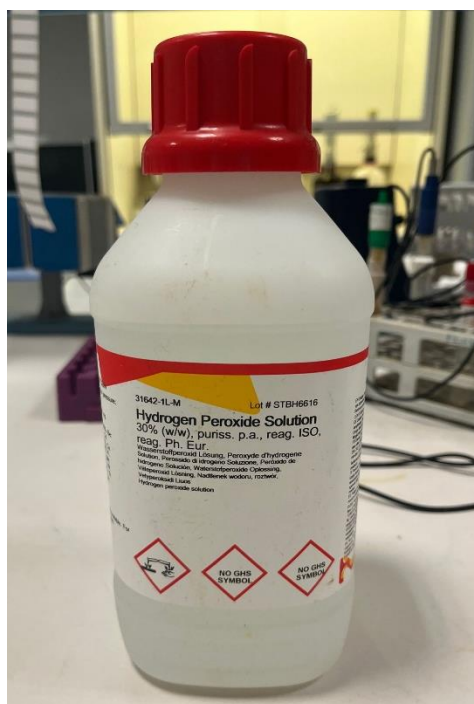


Figure 6. Hydrogen Peroxide Solution from Sigma-Aldrich

Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 99.5-101%) was purchased from Carlo Erba.

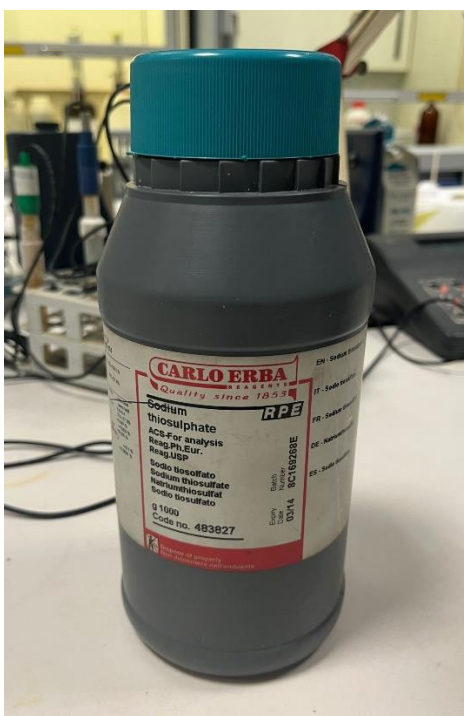


Figure 7. Sodium thiosulfate pentahydrate from Carlo Erba

Sulfuric acid (H_2SO_4 , 95.0-97.0%) was purchased from Sigma Aldrich.

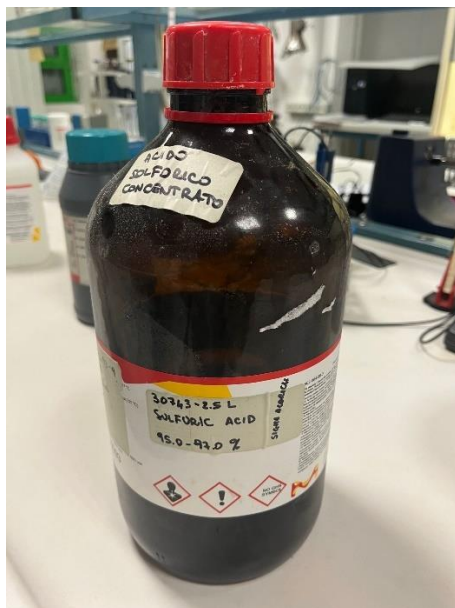


Figure 8. Sulfuric acid from Sigma Aldrich

Sodium hydroxide (NaOH, $\geq 97.0\%$) was purchased from Merck Millipore.



Figure 9. Sodium hydroxide from Merck Millipore

3.2 Methods employed for the experimental thesis

In order to investigate the effectiveness of the Fenton process in the chemical oxidation of methylene blue, a series of experiments were conducted under different operating

conditions. The objective was to evaluate the impact of various parameters on the degradation efficiency and removal of methylene blue from wastewater.

3.2.1 Operating conditions

Batch tests in glass beakers were performed at room temperature and constant stirring, using the same initial concentration of the methylene blue solution (100ppm) and the same amount of methylene blue solution (200ml). The following table shows the operating conditions adopted for the different tests:

Identification	H ₂ O ₂ (mM)	Fe (mM)	Initial pH	Temperature (°C)	Test time (minutes)
Effect of the H ₂ O ₂ concentration	0	0	2,8	25	60
	0,625	0,051	2,8	25	60
	1,25	0,102	2,8	25	60
	2,5	0,204	2,8	25	60
	5	0,408	2,8	25	60
Effect of the Fe ²⁺ concentration	2,5	0	2,8	25	60
	2,5	0,05	2,8	25	60
	2,5	0,1	2,8	25	60
	2,5	0,2	2,8	25	60
	2,5	0,3	2,8	25	60
Effect pf the pH	2,5	0,204	2,8	25	60
	2,5	0,204	5	25	60
	2,5	0,204	1	25	60
	2,5	0,204	7	25	60
1,25 mM H ₂ O ₂ (nanobubbles)	1,25	0,102	2,8	25	60
TOC measurements	2,5	0,625	2,8	25	60
	588	147	2,8	25	7200

3.2.2 UV-vis spectrophotometry method for the measure of the blue methylene concentration

In order to measure the concentration of blue methylene, absorbance measurements at $\lambda=665\text{nm}$ [10] were made by using UV-vis spectrophotometer (Jenway 6715, shown in the image below).



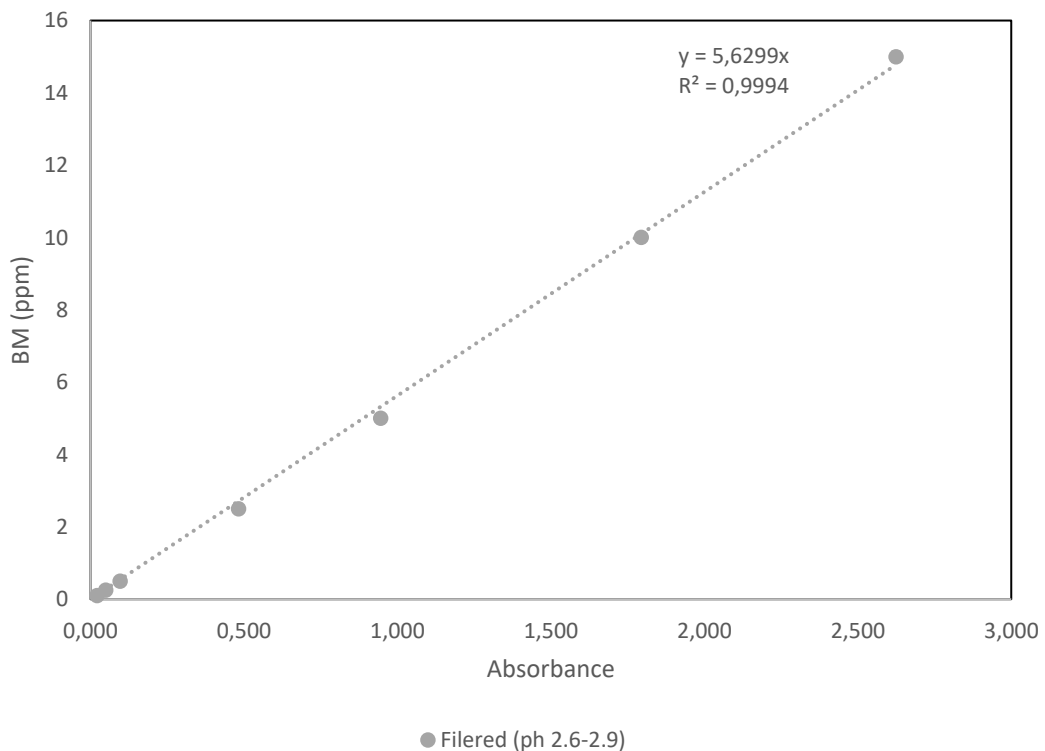
Figure 10. Spectrophotometer from Jenway

The UV-vis spectrophotometer was calibrated with 7 samples of 0.1, 0.25, 0.5, 2.5, 5, 10 and 15 ppm of blue methylene at a pH of 2.6 to 2.9 fixed with a pH meter from Hanna Instruments, by adding drops of diluted (1:2) sulfuric acid (H_2SO_4).



Figure 11. 7 samples of 0.1, 0.25, 0.5, 2.5, 5, 10 and 15 ppm of blue methylene

When the different known standards solutions were prepared, the absorbance of each was measured and they were plot in a graph that compared blue methylene concentration with the absorbance measured. This calibration curve was necessary to calculate the concentration of the blue methylene in ppm of the aqueous solution with the absorbance measurements. The calibration curve graph is described below.



For all of the measurements the samples were taken in duplicate and filtered with a syringe filter of a pore size of 0.45 μm (the filter is shown in the image below).



Figure 12. Syringe filter

3.2.3 Blue methylene decolorization kinetics under different H₂O₂ concentrations

The dosage of Fenton reagents, ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2), affect directly the oxidative capacity of the Fenton process. Different dosages of Fe^{2+} and H_2O_2 were investigated to identify the optimal combination for achieving an efficient methylene blue degradation. The Fe^{2+} dosage was from 0 mM to 0.4 mM, while the H_2O_2 dosage ranged from 0 mM to 5 mM. The applied molar ratio between H_2O_2 and Fe^{2+} was chosen based on previous literature papers (Dutta et al 2001) and was set equal to 12.4.

First, 200 mL of methylene blue solution (100 ppm) was poured into the glass beaker. The pH was then fixed to 2.8 with a pH meter from Hanna Instruments, by adding drops of diluted (1:2) sulfuric acid (H_2SO_4).

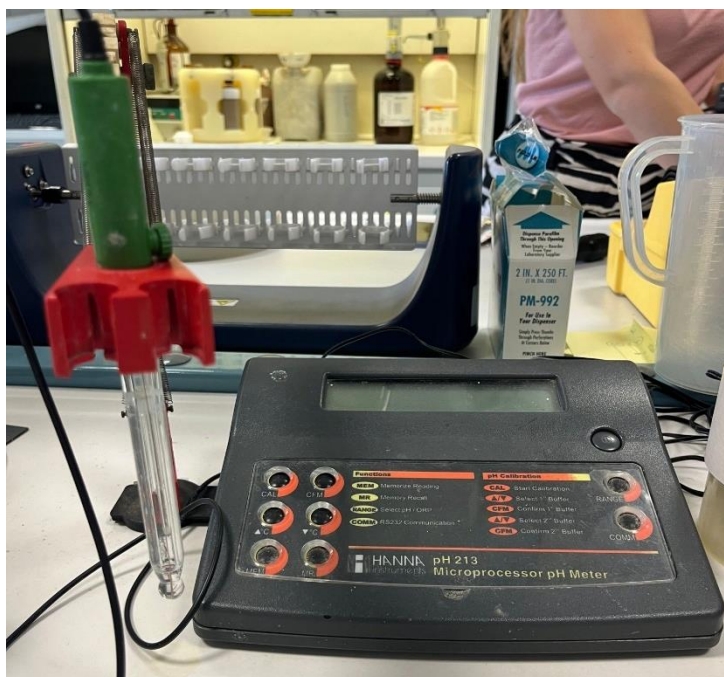


Figure 13. pH meter from Hanna Instruments

Once the solution is prepared, the UV-vis spectrophotometry was used to verify the blue methylene initial concentration. After, the measurements of the absorbance were made in duplicate before the start of the reaction and after 2, 5, 10, 15, 20, 30, 45 and 60 minutes.

3.2.4 Blue methylene decolorization kinetics under different Fe^{2+} concentrations

In this case, with a fixed amount of H_2O_2 , different dosages of Fe^{2+} were investigated to identify the optimal condition for an efficient methylene blue degradation. The Fe^{2+} dosage was from 0 mM to 0.3 mM.

The procedure of this test is similar to the Blue methylene decolorization kinetics under different H_2O_2 concentrations, 200 mL of methylene blue solution (100 ppm) is prepared at a pH of 2.8 by adding diluted sulfuric acid. After, the measurements in the UV-vis spectrophotometry were made in duplicate before the start of the reaction and after 2, 5, 10, 15, 20, 30, 45 and 60 minutes.

3.2.5 Blue methylene kinetics at different pH

The pH of the reaction solution has a profound influence on the Fenton process and its oxidation capability. To explore the impact of pH on the degradation of methylene blue,

the experiments were made at different pH values ranging from acidic to neutral conditions. The pH values tested were 1, 2.8, 5 and 7. By examining the degradation efficiency at different pH levels, the optimal pH range for the Fenton process could be determined, providing insights into the feasibility and effectiveness of this method under various pH conditions.

For the pH measurement kinetics, after preparing the initial solutions, each solution needed to be fixed to the corresponding pH (1, 2.8, 5 and 7) by adding drops of diluted (1:2) sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH at 0.1M) depending on the expected pH, taking the measurements with the pH meter from Hanna instruments named above.

After fixing the pH, the reagents are introduced in the solution to start the reaction, the solution is stirred until the end of the experiment and the measurements of the absorbance are repeated after 2, 5, 10, 15, 20, 30, 45 and 60 minutes. The results were expressed as the ratio of the concentration (C) at a certain time over the initial concentration (C_0).

3.2.6 pH trend in acidic conditions

Also, the pH trend in acidic conditions was analyzed to assess the pH dependency of the reaction and how was the variation of the pH during the reaction, after preparing the initial solutions, each solution needed to be fixed to the corresponding pH (3 and 5) by adding drops of diluted (1:2) sulfuric acid (H_2SO_4).

After fixing the pH, the reagents are introduced in the solution to start the reaction, the solution is stirred until the end of the experiment and the measurements of the pH are repeated after 2, 5, 10, 15, 20, 30, 45 and 60 minutes.

3.2.7 Total organic carbon (TOC) measurements

The Total Organic Carbon (TOC) is a measure of the concentration of organic carbon in a substance and is considered to be the best indicator of contamination of a substance. In order to calculate TOC, you need to measure the Total Carbon (TC) and the Total Inorganic Carbon (IC) in the sample. The TOC value is then calculated using the simple

formula: $TOC = TC - TIC$. [15] The TOC was calculated to study the amount of organic carbon removal during the decolorization process of the blue methylene solution.

For the decolorization kinetics, after preparing the solution it was necessary to fix the pH to 2.8 by adding drops of diluted (1:2) sulfuric acid (H_2SO_4). Once the solution is optimally prepared, the initial TOC measurement was measured, after, the reagents are introduced in the solution. Two tests were studied, the first one measured the degradation of methylene blue in one hour, the second measured the maximum removal that can be obtained in 5 days. In all of the measurements the reaction was stopped with an adequate amount of sodium thiosulfate. The TOC measurements were taken with the total organic carbon analyzer from Shimadzu shown below.



Figure 14. Total organic carbon analyzer from Shimadzu

3.2.8 Nanobubbles generation

Nanobubbles were tested to investigate their possible enhancement of the homogeneous Fenton reaction for the blue methylene decolorization.

The nanobubbles were generated by a meticulous procedure. First, we needed to collect 3 liters of ultra purified water (UP water) generated with the Zeener Power 1 Water Purification System from Human Corporation shown in the image below.



Figure 15. Zeener Power 1 Water Purification System from Human Corporation

Then the water is introduced in the pressure container from Plan B Corporation shown in the figure below.



Figure 16. Pressure container from Plan B Corporation

When the container is closed and it is safe to proceed, the pressure is fixed to 0.3MPa inside the container with a compressor from Plan B Corporation also shown in an image below, this procedure is repeated 10 times to reach an optimal amount of nanobubbles. After, the water is extracted from the pressure container ready to be employed.



Figure 17. Compressor from Plan B Corporation

Once the ultra purified water was prepared with nanobubbles, the solution with 100ppm of methylene blue was prepared, the kinetics for 1.25 mM of H_2O_2 and 0.102 mM of Fe^{2+} was studied as it is described before.

4 Results

In this section, the results achieved in the present study on the kinetics of oxidative decolorization of methylene blue using the Fenton process are presented. Our investigation involved analyzing various initial conditions, including the concentrations of H_2O_2 , Fe^{2+} , and pH. Also, the enhancement potential of the Fenton reaction with nanobubbles was studied. Lastly, we tested the degradation of methylene blue with total organic carbon (TOC) measurements.

4.1 Kinetics for Different Initial H_2O_2 Concentrations

To examine the influence of the initial H_2O_2 concentration in the decolorization of methylene blue with the Fenton process, different tests were conducted.

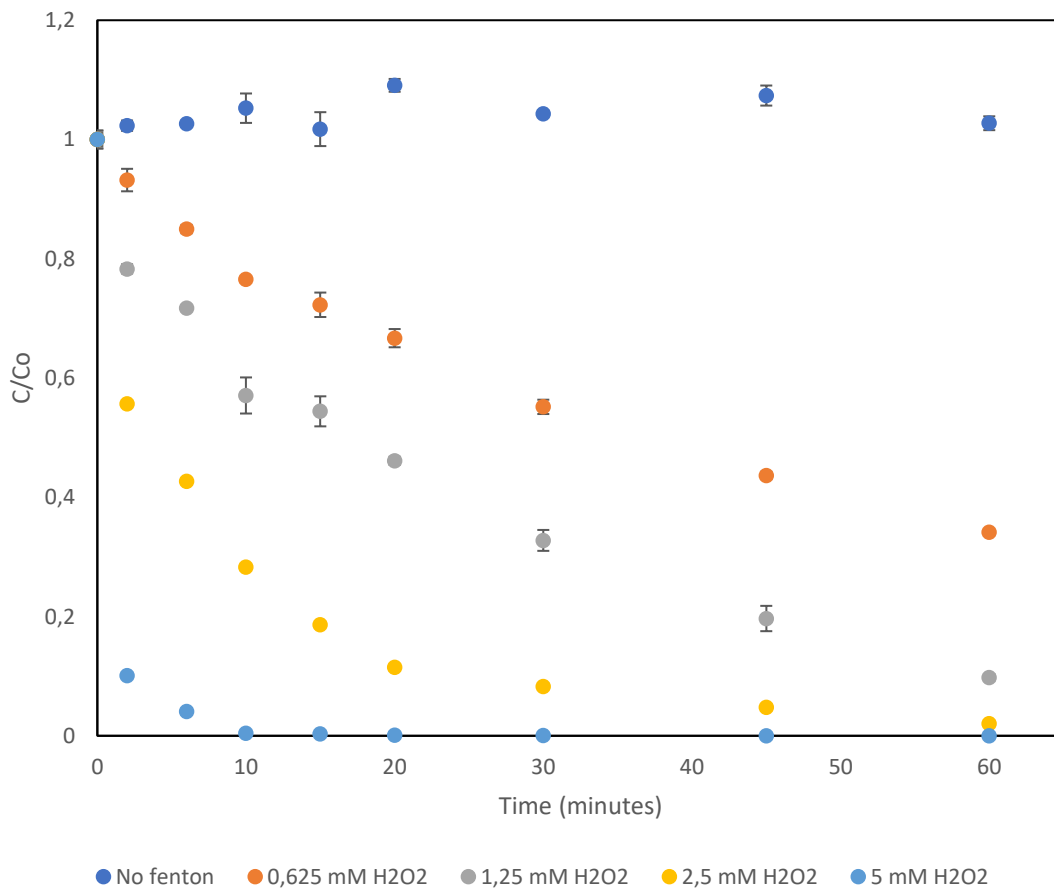


Figure 18. Removal Kinetics for methylene blue applying different H_2O_2 concentration ($\text{H}_2\text{O}_2/\text{Fe}$ molar ratio of 12.4:1)

The results showed a direct relation between the initial H₂O₂ concentration and the rate of methylene blue decolorization. In our tests, the best condition is 5 mM of H₂O₂. As we can see, direct oxidation does not produce any decolorization, therefore hydrogen peroxide needs to be activated. Higher concentrations led to a faster decolorization process; these results highlight the importance of optimizing the H₂O₂ dosage to achieve decolorization rates.

4.2 Kinetics for different initial Fe²⁺ concentrations

The impact of varying the initial Fe²⁺ concentrations with a fixed amount of H₂O₂, on the kinetics of methylene blue decolorization was also studied, experiments were carried out using different Fe²⁺ concentrations from 0 mM to 0.3 mM. Each measurement was performed in duplicate.

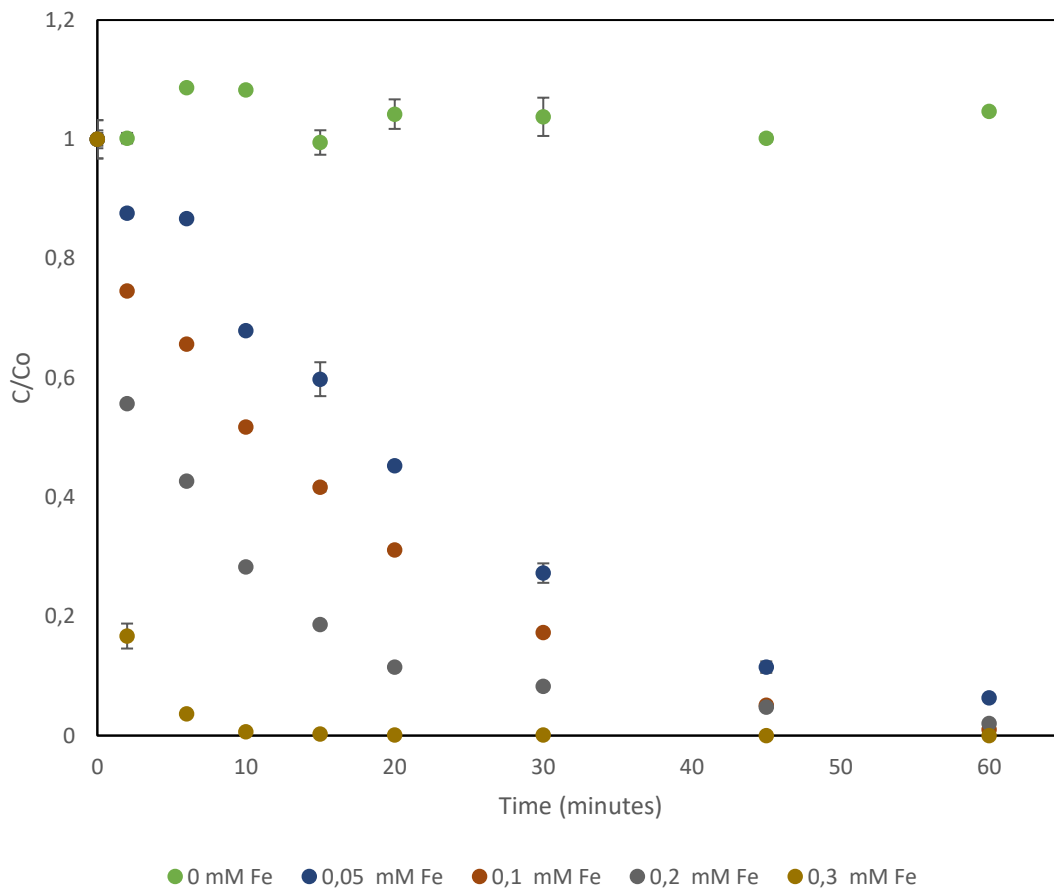
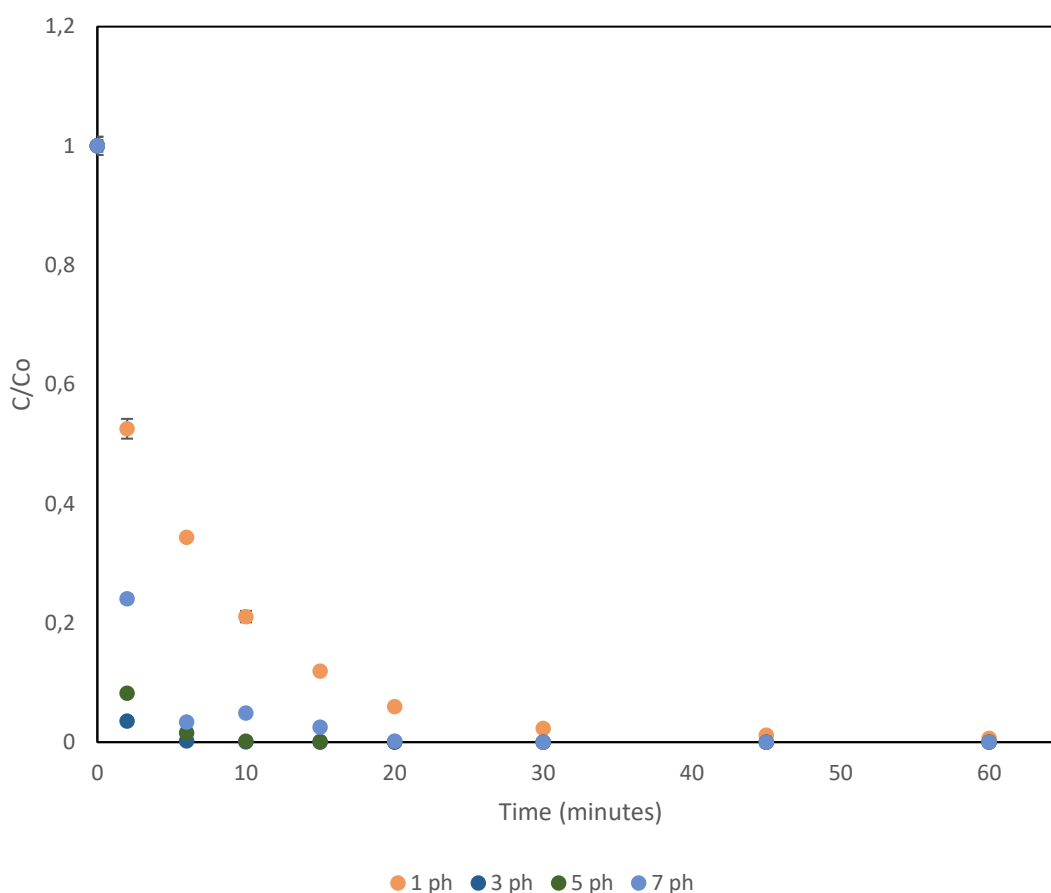


Figure 19. Kinetics for methylene blue with a fixed amount of H₂O₂ and a variation on Fe

The results demonstrated a relationship between the initial Fe^{2+} and the rate of methylene blue decolorization. When the Fe^{2+} concentrations were higher, the decolorization rates increased. In our tests, the best condition is 0.3 mM of Fe^{2+} . These findings highlight the significance of optimizing the Fe^{2+} concentration for effective methylene blue decolorization.

4.3 Kinetics for Different Initial pH Solutions

To explore the influence of the pH of the initial solution on the decolorization rates of methylene blue, different experiments were done using different initial pH values from 1 to 7. Each measurement was performed in duplicate.

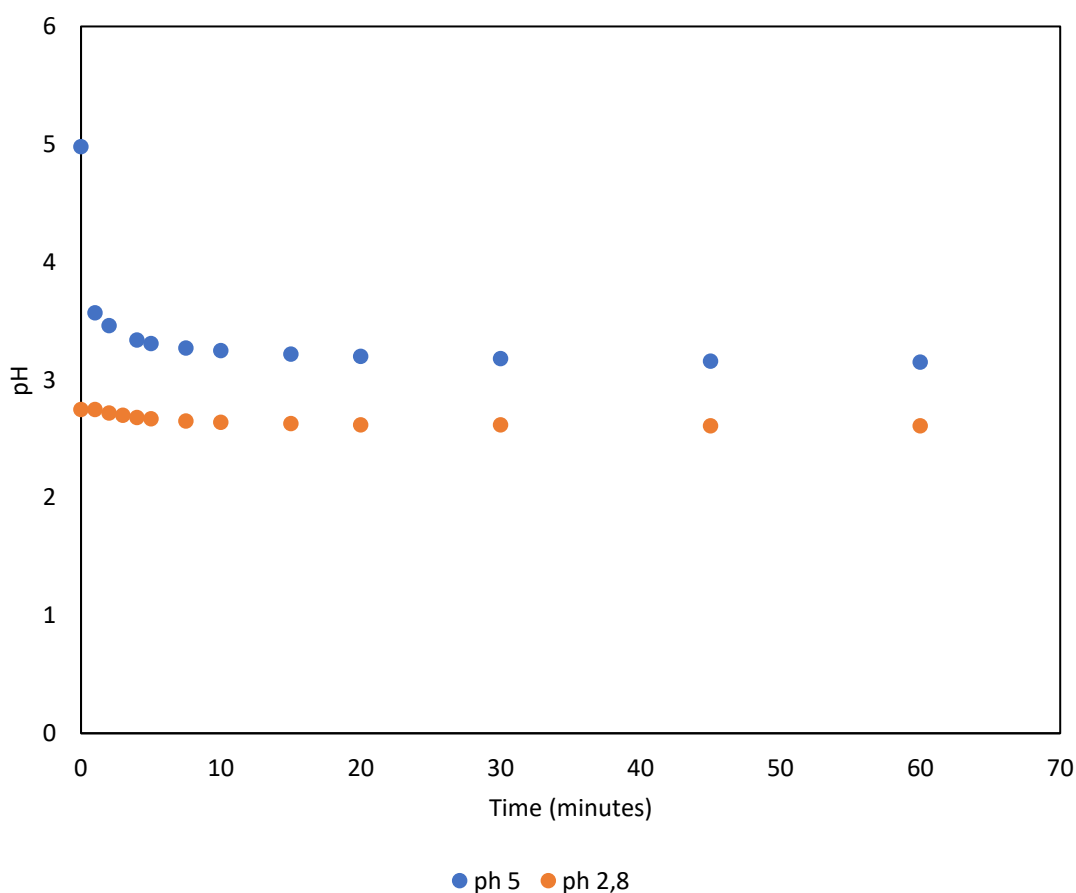


The results revealed that the initial pH significantly affected the decolorization kinetics. Different pH values exhibited distinct rates of decolorization, indicating the pH dependency of the Fenton reaction. The optimal pH was 3, whereas with pH 1 the decolorization rate was slower than the rest of tests. These findings emphasize the

necessity of considering and controlling the pH conditions to achieve optimal decolorization efficiency, in accordance with the results of the literature [16].

4.4 pH trend in acidic conditions

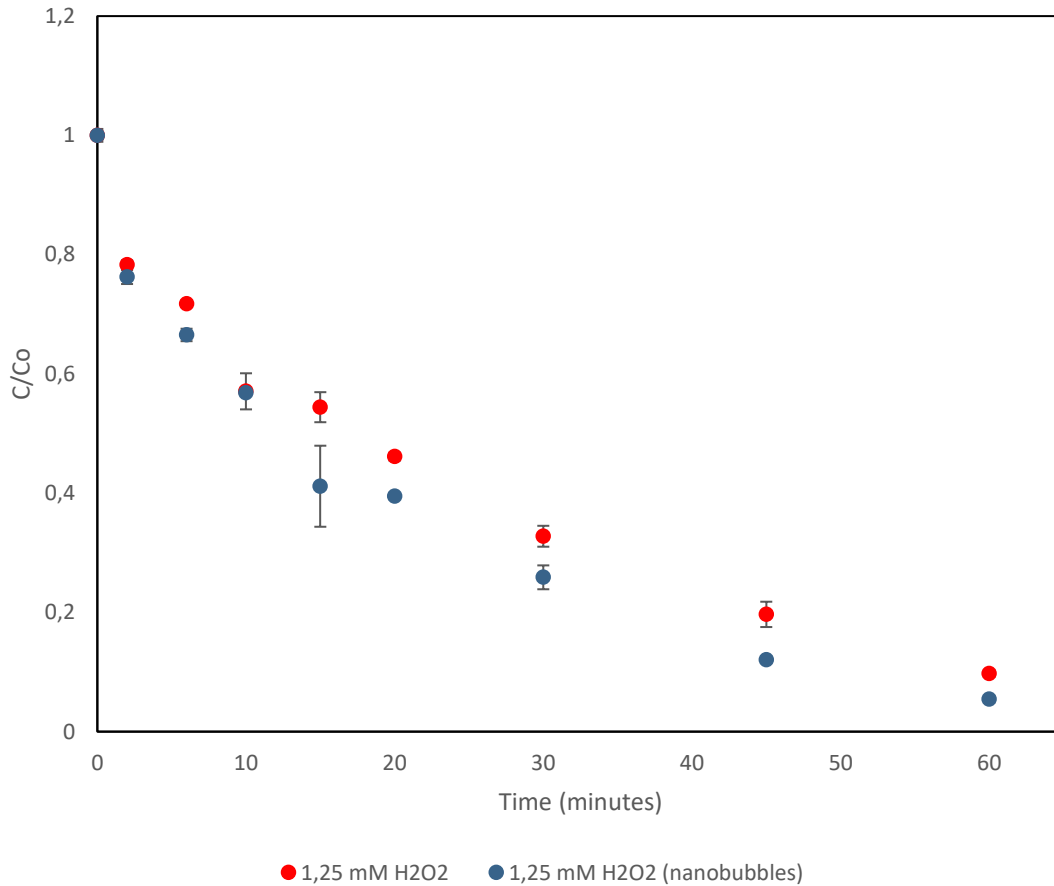
In order to investigate the effect of initial pH solutions on the kinetics of the Fenton reaction, the trend of the pH of the solution with different initial pH was analyzed, these experiments were conducted to assess the pH dependency of the reaction. The pH levels examined were 3 and 5.



The results show that the with the addition of H_2O_2 the pH drops down. Namely, the pH 3 solution decreased a very little amount whereas the pH 5 decreased almost 2, because of the probable formation of acidic subproducts [17].

4.5 Kinetics for 1.25 mM of Initial H_2O_2 Concentration with and without Nanobubbles

To investigate the potential enhancement of the Fenton reaction through the use of nanobubbles, experiments were conducted with a fixed initial H_2O_2 concentration of 1.25 mM, both with and without the presence of nanobubbles, each experiment was performed in duplicate to ensure reliability and validity.



The results didn't demonstrated that the use of nanobubbles in the Fenton reaction led to an improvement in the decolorization kinetics compared to the reaction without nanobubbles. The presence of nanobubbles was supposed to enhance the efficiency of methylene blue decolorization although any conclusive results could be determined from the tests taken.

4.6 TOC Measurements

In addition to studying the decolorization kinetics, we also investigated the degradation of methylene blue using TOC measurements. The TOC analysis allowed us to assess the extent of organic carbon removal during the decolorization process.

The results showed a substantial decrease in the TOC content over time, indicating the successful degradation of methylene blue and the removal of organic carbon, although a complete removal was expected, the tests showed it was only around a 32% after 5 days. Although the measurements of absorbance indicate that the blue methylene decolorization is completed in a short period, the total organic carbon removal is not complete, suggesting that there has been a production of intermediates which could not be oxidized, in accordance with the results of the literature [16].

	Time [minutes]	TC [ppm]	TC Variation	IC [ppm]	IC Variation	TOC [ppm]	Dilution	TOC [ppm]	Removal
$[H_2O_2]/[BM] = 8$ (0.009%)	0	7,578	0,0%	3,013	0,0%	4,5650	10	45,650	0,0%
$[H_2O_2]/[Fe^{2+}] = 4$ [BM] = 100 ppm	30	5,130	32,3%	1,304	56,7%	3,8260	10	38,260	16,2%
	60	4,535	40,2%	0,693	77,0%	3,8420	10	38,420	15,8%

	Time [minutes]	TC [ppm]	TC Variation	IC [ppm]	IC Variation	TOC [ppm]	Dilution	TOC [ppm]	Removal
$[H_2O_2]/[BM] = 1881$ (2%)	0	10,950	0,0%	2,070	0,0%	8,8800	5	44,400	0,0%
$[H_2O_2]/[Fe^{2+}] = 4$ [BM] = 100 ppm	150	4,885	55,4%	1,045	49,5%	3,8400	5	19,200	56,8%
	7200	7,18	34,4%	1,179	43,0%	6,0010	5	30,005	32,4%

5 Conclusion

In conclusion, this experimental thesis presents an investigation into the advanced oxidation of methylene blue using the Fenton process. Through an analysis of various experimental parameters and conditions, including initial H_2O_2 concentrations, Fe^{2+} concentrations, initial pH, and the incorporation of nanobubbles, it was possible to find the optimal conditions for the decolorization of methylene blue.

Our findings showed that with the same molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ higher concentrations of H_2O_2 contribute to a faster decolorization process. In our tests, the best condition is 5 mM of H_2O_2 . These results highlight the critical role of H_2O_2 dosage optimization in achieving desirable decolorization rates in practical applications.

Similarly, the influence of initial Fe^{2+} concentrations on the decolorization kinetics at fixed H_2O_2 concentration was investigated. We have observed a relationship between the initial Fe^{2+} concentration and the rate of methylene blue decolorization. This correlation highlights the importance of optimizing the Fe^{2+} dosage to ensure effective oxidation. In our tests, the best condition is 0.3 mM of Fe^{2+} .

Furthermore, the effect of the initial pH on the methylene blue decolorization was evaluated. Results showed significant variations in the decolorization kinetics as a function of pH, emphasizing the crucial role of pH in dictating the overall efficiency and reaction rates. In our tests, the best condition is a pH of 3. These findings underscore the importance of carefully selecting and controlling the pH conditions in the wastewater treatment to achieve optimal decolorization rates.

Furthermore, this study confirmed the difficulty in completely removing total organic carbon using the Fenton process. Experimental results showed that the maximum removal of TOC was 56.8%. Future research may explore alternative methods or modifications to the Fenton process to enhance TOC removal efficiency in the treatment of wastewater containing methylene blue.

Moreover, our investigation into the utilization of nanobubbles as a potential enhancement in the Fenton reaction hasn't yielded promising results. The kinetics of

methylene blue decolorization with the introduction of nanobubbles hasn't shown a notable improvement compared to the reaction without their presence. The incorporation of nanobubbles should have a further investigation for enhancing the performance and efficiency of the Fenton process in water treatment and environmental remediation applications.

In summary, this research paper contributes to the understanding of advanced oxidation processes, specifically the Fenton process, for the decolorization of methylene blue. The identified correlations between different initial conditions and the decolorization kinetics provide crucial insights for optimizing the process parameters in practical applications.

Future investigations may focus on expanding the application of nanobubbles and better understanding the production of intermediates from methylene blue oxidation as suggested by the total organic carbon measurements. By continuously advancing our knowledge and refining the wastewater treatments, we can contribute to the development of sustainable and efficient solutions for addressing water pollution challenges worldwide.

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