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# Waste-water Treatment on Azo Dyed Water using Fenton Process

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*Abstract:* Textile industries commonly produce wastewater with persistent and potentially toxic azo dyes, posing a significant environmental challenge. This study centres on utilising the Fenton process, an advanced oxidation method, for treating wastewater that includes Direct Blue 15, a prevalent azo dye. The objective is to evaluate the Fenton process's effectiveness in breaking down Direct Blue 15 and improving overall water quality. Quantitative analysis, employing UV-Vis spectrophotometry , tracked the extent of azo dye degradation and overall enhancement in wastewater quality. Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$) was used as the $Fe^{2+}$ source, while hydrogen peroxide ($H_2O_2$) served as the primary source of hydroxyl radicals ($OH{\cdot}$) for the reaction. Sulfuric acid ($H_2SO_4$) was added to the initial pH as needed. Samples with varying concentrations of azo dye, $FeSO_4{\cdot}7H_2O$, and $H_2O_2$ were prepared and treated through the Fenton process. A calibration curve was constructed using UV spectroscopy to quantify the remaining dye concentration in the treated samples. The project's objectives are to ascertain the Fenton process' effectiveness in eliminating azo dyes from wastewater and maybe optimise process parameters for better treatment.

***Index Terms* - Azo dyes, Fenton process , Direct blue 15 , UV spectrophotometry, Wastewater, Calibration Curve**

## I. INTRODUCTION

Industries, which are often associated with creativity and efficiency, consistently produce wastewater that is full of various contaminants. In order to promote sustainable industrial practices, it is strategically critical to handle this effluent in a way that goes beyond simple regulatory compliance. The implications of wastewater management cut across industries, including resource conservation, environmental compliance, and the fundamental commitment to ecological preservation.

The word "azo dye" refers to a wide range of artificial organic substances that are identified by the distinctive azo group that joins two carbon-containing moieties. Because of its great colour range and stability, this adaptable class of dyes has found uses in textiles, plastics, cosmetics, and other industries. But the very molecular resilience that makes azo dyes appealing to industry also makes them resistant to easy degradation, which begs the question of how long they will last in environmental matrices.

Azo dyes, which are essential to industrial colouring, capture the delicate equilibrium between development and environmental consciousness. Direct Blue 15 perfectly captures this dynamic with its captivating blue grace. The wastewater produced when industries take advantage of these colours' brightness becomes a focal point for environmental concerns. Because of Direct Blue 15's molecular complexity, standard degradation techniques are put to the test, necessitating a careful approach to wastewater treatment. This study takes a multimodal approach to unravel the robustness of Direct Blue 15 in wastewater by the powerful Fenton process with accurate use of UV-Vis spectrophotometry. The Fenton process, which produces hydroxyl radicals using hydrogen peroxide and iron catalysts, provides a customised approach in the search for sustainable solutions.

In addition, UV-Vis spectrophotometry functions as an advanced instrument that offers instantaneous insights into the dynamics of Direct Blue 15 degradation during treatment. The Fenton procedure offers an environmentally friendly and efficient way to deal with the resistant properties of azo dyes.It creates highly reactive hydroxyl radicals by combining hydrogen peroxide and ferrous ions. It creates highly reactive hydroxyl radicals by combining hydrogen peroxide and ferrous ions. This method of oxidation has demonstrated a great deal of effectiveness in breaking down complex organic pollutants, including azo dyes, into less harmful byproducts. Fenton chemistry's introduction into wastewater treatment is a natural fit with the growing emphasis on ecologically friendly and environmentally conscious technology. Adding spectrophotometry to this model enhances our understanding and analytical skills. Methods such as UV-Vis spectrophotometry are essential for monitoring the deterioration process, evaluating the effectiveness of azo dye removal, and identifying intermediate products. As we embark on this study, our focus is on exploring the combined efficacy of the Fenton process and spectrophotometry, specifically targeting the removal of Direct Blue 15, a prevalent azo dye, from wastewater. By investigating optimal operating conditions, assessing degradation efficiency, and employing advanced spectrophotometric analyses, this research aims to contribute valuable insights toward the advancement of sustainable water treatment strategies in the presence of azo dyes.

The landscape of related work unveils a meticulous exploration of strategies aimed at addressing the formidable challenge posed by azo dyes in wastewater treatment, with a discernible focus on the recalcitrant nature of Direct Blue 15. The scholarly pursuit of understanding and mitigating the environmental impact of this prominent azo dye encompasses a spectrum of investigations[1].The mineralization of AR18 under electro-Fenton conditions is significantly influenced by operational parameters such as pH, applied current, supporting electrolyte, and $H_2O_2$ concentrations. The oxidation process of AR18 by hydroxyl radicals exhibits pseudo first order kinetics. AR18 and related components can be operationally removed from industrial effluent using the electron-Fenton technique[2].Metal ion catalytic activities were compared, with Fe2+ demonstrating the highest efficacy. The investigation also evaluated three other oxidation processes, emphasising the higher effectiveness of $Fe^{2+}$/ $H_2O_2$/UV, suggesting that ultraviolet light and ferrous ions work in concert to accelerate the degradation process[3]. The eco-friendly coagulation/flocculation approach proves effective for decolorizing industrial wastewater, making it reusable. In this approach, the focus is on removing disperse red 17 dye (DR 17) while maintaining a constant initial dye concentration of 60 mg/L. Operational parameters, including the type and dosage of oxidants (hydrogen peroxide, ferric chloride, alum, and Corchorus olitorus), were examined for their impact on colour removal efficiency[4]. Because there is more iron available under homogeneous conditions, primary degradation (decolorization) and mineralization ($CO_2$ and $H_2O$) proceed much more quickly. The iron's status is the primary distinction: both in solution and fixed in heterogeneous catalysis[5]. The creation of a brand-new iron-based metal-organic framework (MOF) catalyst that can efficiently break down methylene blue at 500 parts per million concentration via a heterogeneous Fenton oxidation process. The methodology entails examining the kinetics of adsorption of MIL-100(Fe) and FeII@MIL-100(Fe), emphasising the influence of electrostatic interactions and surface area[6]. Using the photo-Fenton technique, a cheap, recyclable, and eco-friendly catalyst was investigated and found to be effective in removing a reactive azo dye from water. However, it's important to consider the acidification cost in potential large-scale applications when comparing this method with established ones. [7]. Cations like $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$ in wastewater can cause cathodic salt precipitation, hindering active sites and reducing H2O2 generation. This impact on the cathode's lifespan necessitates effective strategies, particularly for scale-up applications. However, a detailed exploration of cation effects in the double layer within the EF process is still pending. [8]. Two inquiry techniques, conductometry and spectrophotometry, were used to examine the interaction between dye. After micro-filtering Direct Blue Dye at molar ratios of 1:4 and 1:8, it achieved a 100% purification rate[9]. Eggshells are a cheap, natural material that can be used to remove DB dye from water and waste water effluent from textile manufacturers.Using a pseudo-second order kinetic model, the DB dye was able to bond to eggshell, demonstrating that chemisorption is what propels the adsorption process.This procedure removes DB dye by 83% and 84.323%, respectively[10].

Hence , the literature review elucidates the efficacy of the Fenton process for treating azo-dyed wastewater.Optimal operational parameters are identified as critical for enhanced efficiency. The review underscores the importance of practical considerations, including the influence of ions and potential byproduct formation.

Azo dyes are a major source of environmental pollution due to their widespread use in industries and their persistence in wastewater. Conventional wastewater treatment methods often struggle to effectively remove these dyes. Therefore, there is a need for developing and investigating efficient and environmentally friendly methods for treating azo dye-contaminated wastewater. Because Direct Blue 15 is so robust, its leakage into industrial effluent presents a significant environmental risk. Water pollution arises from the inadequacy of current treatment methods. It is very necessary to use advanced techniques created especially for Direct Blue 15's unique characteristics.

## II. Research Methodology

A. Fenton Process

The fenton process is an effective advanced oxidation method that creates highly reactive hydroxyl radicals by reacting ferrous ions (Fe2+) with hydrogen peroxide (H2O2). This oxidative technique successfully breaks down persistent organic pollutants, particularly azo dyes, into less harmful byproducts. Fenton chemistry aligns with the increasing focus on sustainable and eco-friendly water treatment technologies. One of the most important phases of the Fenton reaction is the generation of hydroxyl radicals (·OH), which are extremely reactive molecules with potent oxidising agents. This occurs through the interaction of Fe2+ ions with hydrogen peroxide (H2O2), as represented by the following equation:

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

The formation of hydroxyl radicals is favoured at acidic pH conditions (pH 2-4), where ferrous ions are more stable and hydrogen peroxide is less prone to decomposition into water and oxygen.

B. Spectrophotometry

Spectrophotometry plays a pivotal role in monitoring chemical reactions and quantifying substance concentrations in a solution. UV-Vis spectrophotometry, commonly used in wastewater treatment, relies on the absorption of light at specific wavelengths by molecules, facilitating the quantitative measurement of chemical concentrations. In the examination of azo dyes like Direct Blue 15, spectrophotometry becomes essential for tracking the degradation process, evaluating removal efficiency, and characterising intermediate products. The wavelength used for the calibration curve was 566 nm.

C. Beer's Law: The relationship between a solution's solute concentration and the amount of light it absorbs is described by Beer Lambert's Law, sometimes referred to as Beer's Law. In the context of spectrophotometry, which measures a sample's light absorbance to determine its concentration, this law is especially crucial.

D. Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$)

The chemical compound ferrous sulphate, or $FeSO_4 \cdot 7H_2O$, is essential to the Fenton reaction. It is a source of ferrous ions ($Fe^{2+}$) and it begins to produce hydroxyl radicals when it combines with hydrogen peroxide.

This catalyst is central to the oxidative degradation of pollutants, including azo dyes. In the context of this research, the concentration and addition of ferrous sulphate are carefully regulated to optimise the Fenton process for efficient removal of Direct Blue 15.

E. Sulfuric Acid ($H_2SO_4$) Sulfuric acid, denoted as H2SO4, is commonly utilised for pH adjustment in the Fenton process. pH control is critical as it influences the efficiency of the reaction. For treating wastewater with azo dyes like Direct Blue 15, maintaining an acidic environment is typically preferred. Sulfuric acid is added to achieve and sustain the desired pH level throughout the Fenton process, ensuring optimal conditions for the degradation of pollutants and maximising treatment efficacy.

## PROCESS DESCRIPTION

The Fenton process for the same two sets of conditions as in the magnetic stirrer process is experimented and analysed on a UV spectrophotometer. At the initial stage of the project, the focus is to analyse the effects of parameters on the Fenton process. Precisely, changing H2O2 : FeSO4 ratio and adjusting pH is a main task. The dye concentration after each treatment was measured using a spectrophotometer UV–Vis at an wavelength of 565 nm (determined experimentally using UV–Vis spectra of the dye). The Fenton process was carried out using samples of 250 mL of DB15 solutions and with different concentrations. The samples were analysed on a UV spectrophotometer of 10mm cells. Each time of run calibration curves are plotted and the unknown concentrations of dye samples are found. Meanwhile, the introduction of $H_2O_2$ triggers a Fenton reaction, in which the presence of $Fe^{2+}$ ions causes $H_2O_2$ to deteriorate and transform into the OH^ radical.

In fig1.1, it has been observed that for around 1hr and more, the maximum degradation was obtained to be 40% with a constant pH of 9. Here we have not introduced the Fenton reagents which can lead to more % of degradation of solution.

| Sample no. | Conc. (ppm) | pH | Degradation (%) |
|---|---|---|---|
| 1. | 25 | 4 | 42 |
| 2. | 23 | 3 | 48 |
| 3. | 24 | 4 | 41 |
| 4. | 25 | 3 | 40 |
| 5. | 26 | 4 | 43 |

*Table 1.1. Observation of magnetic stirrer experimental run for acidic solution($H_2O_2^-$), with a pH range of 3-4 for 1 hr.*

**Degradation Of dye solution with Fenton reagents and $FeSO_4$ :**

After the treatment of dye solution with $H_2O_2$, we were introduced with FeSo4 solution on magnetic stirrer. Here the pH of solution was maintained at 2 for 60 min, with different concentrations for better results of degradation.

Similarly , in fig 1.3 , we can see that the addition of Acidic solution increases the percentage of degradation to 48 %.The degradation pattern is highly acidic and lean $H_2SO_4$ is low. The rate of reaction decreases significantly. For the same period of 60 min as that of the basic solution, the degradation is approximately 30-35 %. Thus pH in the range of 3-7 would appreciate to get high concentration of hydroxyl radicals and thereby will increase the degradation and rate of degradation.

The overall reaction involves the oxidation of the dye by hydrogen peroxide and the reduction of the dye by ferrous sulphate. The hydrogen peroxide breaks down into water and oxygen, and ferrous sulphate to be oxidised to ferric sulphate.

This treatment helped us to achieve a maximum 90 % of degradation and decolorized the dye solution.

For basic solutions, % Degradation achieved at constant 9 pH and 1 hr run time is given in *Table 1.2*

| Conc. (ppm) | % Degradation |
|---|---|
| 05 | 40 |
| 10 | 36 |
| 15 | 33.3 |
| 20 | 25 |
| 25 | 20 |

*Table 1.2. Observation of dye solution with $H_2SO_4$ with different concentrations.*

## III. Result and Discussion

The result given by the UV-Spectrophotometer as in the graph in fig 1.2

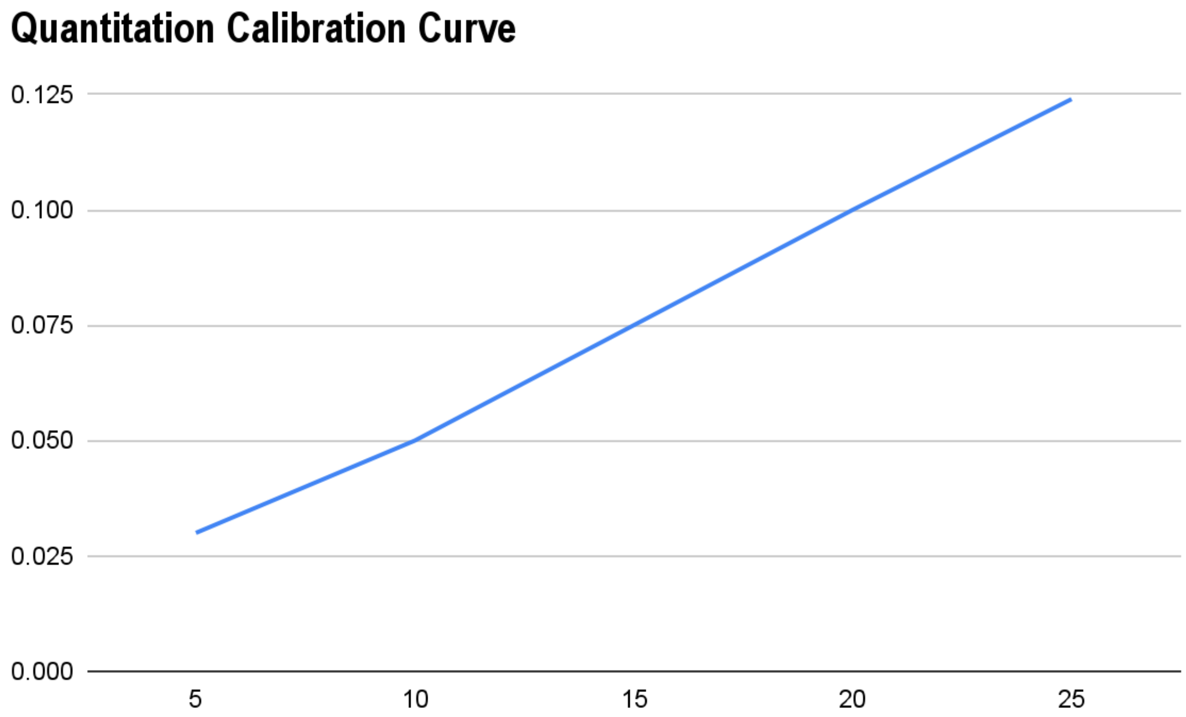


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*Fig 1.2. Graph: Calibration curve: Absorbance vs. Concentration(mg/L)*

From Beer Lambert's Law, we get to know about the Absorbance of the unknown sample which was **0.00407318 $M^{-1}cm^{-1}$**

At end by using Beer's Lambert law we got the concentration of unknown samples, which was by the slope **y = mx + c,** concentration was;

| Absorbance | Concentration (ppm) | % Degradation |
|---|---|---|
| 0.029 | 5.405125725 | 21.62 % |
| 0.054 | 11.54283631 | 50.19 % |
| 0.067 | 14.73444581 | 61.38 %o |
| 0.096 | 21.85419009 | 87.4 % |
| 0.108 | 24.80029117 | 95.38 % |

*Table 1.3. Concentration of unknown sample*

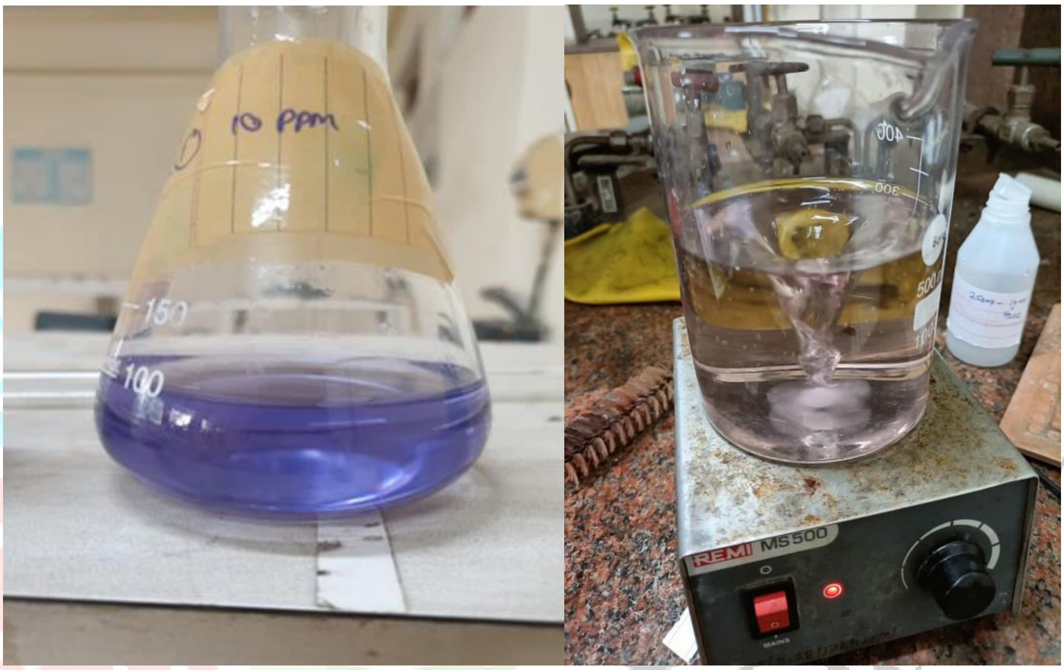


*Fig.1.3 (a) Color change after adding fenton reagents of first sample (b) Color change after adding fenton reagents of last sample*

Fig.1.3(b) is the colour change of the mixture after adding fenton reagents. This hue shift represents the dye's degradation and removal, demonstrating the Fenton process's capacity to handle and clean up wastewater contaminated by color-giving materials like industrial dyes. The continual observation and analysis of this colour transformation offer valuable insights into the performance of the Fenton process, particularly in addressing the issues of water pollution linked to coloured pollutants.

## IV. Conclusion

The experimental setup, with optimised Fenton process parameters, facilitated precise assessment of Direct Blue Dye removal kinetics. Controlled introduction of Hydrogen Peroxide and vigilant reaction time monitoring highlighted the need for accuracy in Fenton process application. Spectrophotometer-based sample analysis ensured precise dye concentration measurement, aiding robust data analysis. The plotted graphs depicted kinetics provided a comprehensive evaluation of the Fenton process. Monitoring confirmed the Fenton process's effectiveness in treating wastewater until the dye concentration reached an acceptable level, ensuring environmental safety. The study concluded by examining the Fenton process's potential as a means of eliminating Direct Blue dye from industrial wastewater. It was shown through a series of methodical tests and analysis that the Fenton reaction is effective at breaking down the complex colour molecules. The dye's structural integrity was broken down by the production of hydroxyl radicals, which resulted in the dye's breakdown into simpler and less hazardous metabolites. The optimization of key parameters, including pH, concentrations of $H_2O_4$ and $Fe_2SO_4$, and reaction time, had an essential role in enhancing the performance of the Fenton method for dye removal. Moreover, the exploration of reaction kinetics provided valuable insights into the degradation pathways, contributing to a deeper understanding of the chemical mechanisms involved.

While the Fenton process exhibited promising results in removing Direct Blue dye, further research should focus on addressing challenges such as byproduct formation and scaling up the process for practical applications in large-scale wastewater treatment facilities. To guarantee the treated effluents' overall environmental safety, intermediary byproducts must be identified and treated. Overall, this study highlights the Fenton process's potential as a successful and environmentally friendly method for cleaning wastewater contaminated with Direct Blue dye. Implementing optimized Fenton-based treatment strategies holds promise for mitigating the detrimental impact of industrial dye discharge on water ecosystems, aligning with the broader objectives of sustainable environmental stewardship. In summary, this study affirms the Fenton process as an eco-friendly method for Direct Blue Dye removal, offering insights valuable for industries addressing wastewater treatment challenges. The findings contribute to the development of sustainable treatment strategies, marking progress in environmental stewardship against industrial dye impact on water ecosystems.

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