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Fenton Reagent-Based Advanced Oxidation for the Degradation of Reactive Black 5 and Methylene Blue Dyes

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Abstract: This study investigates how Fenton oxidation affects the decolourization and mineralization of two dyes—an azo dye (Reactive Black 5) and a basic dye (Methylene Blue)—in water. A series of batch experiments were conducted to determine the optimal conditions for the process, including the starting concentrations of the dyes, dosages of hydrogen peroxide (H_2O_2) and ferrous sulfate ($FeSO_4$), pH levels, reaction time, and temperature. The degradation of both dyes was assessed by measuring the extent of color removal and mineralization, using UV-visible spectrophotometry and chemical oxygen demand (COD), respectively. The most effective conditions were found to be at a pH of 3 and a temperature of 40°C, with 200 mg/L of Reactive Black 5 and 150 mg/L of Methylene Blue. For Reactive Black 5, the use of 30 mg/L $FeSO_4$ and 300 mg/L H_2O_2 achieved 99.32% color removal, while 50 mg/L $FeSO_4$ and 500 mg/L H_2O_2 resulted in 99.28% color removal for Methylene Blue after 25 minutes of treatment. COD reduction was 60% for Reactive Black 5 and 73.33% for Methylene Blue. These results indicate that the Fenton process can achieve nearly complete decolourization and significant, though partial, mineralization. Further analysis using GC-MS confirmed the breakdown of the dyes and showed the absence of certain toxic by-products after the treatment.

Keywords: *Advanced Oxidation Process, Fenton Reagent, Kinetics, Thermodynamics.*

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I. INTRODUCTION

The earliest recorded use of an organic dye dates to approximately 4,000 years ago, when indigo was detected in the textile wrappings of mummies in ancient Egyptian tombs (Berton & Gordon, 1983). In contemporary industrial applications, synthetic dyes are employed extensively across various sectors, including textiles, food production, pharmaceuticals, cosmetics, leather processing, and paper printing. Among these, the textile industry is the largest consumer of dyes (Silveira, Marques, & Silva, 2009). Despite their widespread use and aesthetic function, dyes represent a significant environmental concern. Even at low concentrations, they are highly visible in water and may exhibit toxicity toward aquatic organisms (Banat, Nigam, & Singh, 1996). Moreover, the presence of dyes in aquatic systems can disrupt ecological processes by limiting light penetration, thereby impairing bacterial activity and inhibiting photosynthesis in aquatic flora (Robinson, McMullan, & Marchant, 2001). Consequently, the removal of dyes from industrial effluents prior to discharge is imperative in wastewater treatment to mitigate their environmental impact. Conventional dye removal strategies involve a combination of physical, chemical, and biological approaches (Chatha, Asgher, & Ali, 2012).

The development of efficient wastewater treatment technologies is essential for sustainable water resource management and environmental protection. Since the 1990s, advanced oxidation processes (AOPs) have emerged as promising techniques for the degradation of hazardous substances in wastewater (Sun *et al.*, 2007). These processes operate through the in situ generation of highly reactive hydroxyl radicals (•OH), which exhibit strong oxidative potential capable of breaking down a wide variety of organic pollutants in both water and wastewater systems (Sun *et al.*, 2007; Zhou, Lu, & Wang, 2009; Lucas & Peres, 2006). A key advantage of AOPs over conventional treatment methods is their ability to achieve complete mineralization of contaminants, effectively converting them into harmless end products (Kdasi, 2004). Moreover, AOPs are recognized as environmentally friendly technologies, as they typically produce minimal secondary waste and rely on transient, high-energy oxidizing species to dismantle complex chemical structures. Among the various AOPs, Fenton's reagent—a homogeneous catalytic system composed of hydrogen peroxide and ferrous ions under acidic conditions—is widely studied. This process generates hydroxyl radicals through a redox reaction mechanism, enabling the oxidation of a broad spectrum of organic compounds (Meric, Kaptan, & Olmez, 2004).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} + HO^{\cdot} \quad (1)$$

Dyes are coloured, ionizing and aromatic organic compounds used to impart permanent colour to other substances. Its most importance use is in colouring textile fibres. Globally, there are over 100,000 commercially available dye types, with an estimated annual production volume of approximately 800,000 tons (Silveira, Marques, & Silva, 2009). Due to the low efficiency of dyeing and finishing processes, more than 150,000 tons of these dyes are discharged into the environment through industrial wastewater. India ranks as the second-largest exporter of dyes, following China. The textile industry primarily relies on synthetic organic dyes, including direct, reactive, and processing dyes. As noted by Mathur, Bhatnagar, and Bakre (2006), environmental concerns related to the manufacture and application of these dyes have escalated significantly in recent decades and now represent one of the most critical challenges shaping the modern textile dye industry.

The term *natural dye* refers to coloring agents derived from natural sources such as plants, animals, and minerals. These dyes are typically non-substantive and require the use of mordants—commonly metallic salts—to facilitate binding between the dye molecules and textile fibers (Samantha & Agarwal, 2009). While their application is more limited, natural dyes are still primarily used in industries such as food processing.

In contrast, synthetic dyes are widely utilized across various industrial sectors, with the textile industry being the largest consumer (Keharia & Madamwar, 2003). The first synthetic organic dye was produced in 1871 when picric acid was synthesized by treating indigo with nitric acid. Since that time, numerous synthetic dyes have been developed and added to the growing list of commercially used colorants (Mathur, Bhatnagar, & Bakre, 2006). These synthetic dyes are increasingly regarded as emerging pollutants due to their potential toxicity and frequent detection in aquatic environments. Despite their environmental presence, there are currently no formal regulations establishing safe concentration limits in water to protect aquatic ecosystems and human health (ETAD, 2013).

Among the various synthetic dye classes, azo dyes—derived from specific aromatic amines—are the most commonly used, particularly in textile applications. The textile sector alone accounts for nearly 70% of global dye consumption, with reactive, vat, and azo dyes being the most prevalent for dyeing and printing cotton fabrics (Walters, Santillo, & Johnson, 2005).

Disperse dyes hold the largest share of the dye market, accounting for approximately 21%, followed by direct dyes at 16% and reactive dyes at 11%. Although disperse dyes are sparingly soluble in water, they are commonly formulated with surfactants to enhance application to synthetic fibers, which enables their persistence in aquatic environments. Maguire (1992) reported that certain disperse dyes have been detected in water bodies, and their occurrence has been associated with mutagenic activity in both water and sediment samples.

- ➢ *Dyes in Textile Industries*

The textile industry is one of the oldest and most dye-intensive sectors globally, utilizing a vast array of coloring agents to meet the growing demand for diverse and aesthetically appealing fabric shades. Textile dyes represent a substantial segment of industrial chemicals, encompassing more than 8,000 individual compounds and approximately 40,000 commercial dye formulations. As consumer demand continues to rise, textile production has expanded correspondingly, contributing significantly to the global dyestuff market—accounting for nearly two-thirds of its total volume. It is estimated that over 10,000 dyes are used exclusively within the textile sector, with azo dyes comprising nearly 70% of these due to their complex synthetic structures (Hassaan, 2016).

Textile manufacturing processes are resource-intensive, requiring large volumes of water, energy, and chemicals, which in turn generate considerable quantities of liquid waste. For instance, producing one meter of finished fabric may require between 12 and 65 liters of water, while manufacturing enough fabric to upholster a single sofa can consume approximately 12,500 liters. A major environmental concern arises from the direct discharge of untreated effluents into natural water bodies. These effluents are often laden with both organic and inorganic pollutants, and appropriate treatment—whether biological, chemical, or physical—is essential prior to release (Elliott, Hanby, & Malcolm, 1954). In addition to water pollution, the textile sector contributes to air contamination through gas emissions and malodorous compounds.

During the dyeing process, not all of the applied dye binds to the fabric. A portion—typically 10–25%—remains unfixed and is subsequently released into wastewater streams. As a result, textile effluents often contain high concentrations of residual dyes, contributing significantly to aquatic pollution. Estimates suggest that approximately 280,000 tons of dyes are discharged annually from textile industries worldwide (Jinx, Liu, & Xu, 2007). These pollutants adversely affect aquatic ecosystems by limiting light penetration, which disrupts photosynthesis and negatively impacts aquatic flora and fauna. In addition, the presence of dyes in water bodies poses risks to human and animal health. The composition and toxicity of textile wastewater vary depending on the raw materials and specific chemicals used in each production cycle, which often change according to customer requirements (Parvathi, Maruthavanan, & Prakash, 2009).

Textile dyes can be classified based on their chemical structure and fiber compatibility into various categories, including acid dyes, direct dyes, azoic dyes, disperse dyes, sulfur dyes, reactive dyes, basic dyes, oxidation dyes, mordant (chrome) dyes, vat dyes, fluorescent brighteners, and solvent dyes. For practical purposes, these can be broadly grouped into three functional categories: dyes for cellulose fibers, dyes for protein fibers, and dyes for synthetic fibers.

II. MATERIALS AND METHODS

➢ *Materials*

All the reagents used are of analytical grade and purchased from sigma-Aldrich which includes: Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), Hydrogen peroxide 30% w/v (H_2O_2), NaOH, H_2SO_4 and De-ionized water. The dyes used were Reactive Black 5 and Methylene blue. The common laboratory apparatus and glassware used includes; conical flask, volumetric flask, spatula, pH meter, measuring cylinder, plastic syringe etc. The analytical instruments used include water-bath shaker, JENWAY 7305 Spectrophotometer, Ohaus weighing balance and GCMS-QP2010SE SHIMADZU, JAPAN.

➢ *Sample Preparation*

Previous research has indicated that effluents from textile industries contain a variety of dyes, with concentrations that differ depending on the specific processes employed (Alaton & Schmidt, 2008). In this study, a dye stock solution was prepared under controlled laboratory conditions, and working standard solutions ranging from 50 to 300 mg/L were obtained through serial dilution of the stock solution.

➢ *Fenton Process Procedures*

Batch experiments employing the Fenton oxidation process were conducted in conical flasks under varying operational conditions, including hydrogen peroxide concentrations ranging from 100 to 500 mg/L, ferrous sulfate dosages between 10 and 100 mg/L, pH levels from 2 to 8, and temperatures spanning 20°C to 50°C. The solution pH was adjusted using 0.5 M sulfuric acid and 1 M sodium hydroxide. Once the optimal pH was identified, the influence of individual parameters was examined by altering one variable at a time while maintaining the others constant (Fongsatitkul, Elefsiniotis, & Yamasmit, 2004).

A dye stock solution was prepared by dissolving a measured quantity of the dye in deionized water. From this stock, a series of working standard solutions with dye concentrations ranging from 50 to 300 mg/L were prepared and used to construct a calibration curve. The dye solutions were agitated on a mechanical shaker at 150 rpm for 30 minutes to ensure proper mixing (Zhou, Lu, & Wang, 2009). After treatment, the pH of the supernatant from each flask was neutralized to approximately pH 8 using 1 M NaOH, prior to further analysis (Tantak & Chaudhari, 2006; Jozwiak, Wiktorowski, & Debicka, 2004).

The pH of all samples was monitored using a digital pH meter, calibrated with standard buffer solutions of pH 4, 7, and 10 at room temperature. Dye concentrations were quantified using a JENWAY 7305 spectrophotometer, with maximum absorbance wavelengths (λmax) of 594 nm for Reactive Black 5 and 664 nm for Methylene Blue. Calibration curves were developed using standard dye solutions of known concentrations to ensure analytical accuracy (Sun *et al.*, 2007).

For each reaction, a measured volume of dye solution was transferred into a conical flask, the pH was adjusted to 3 with 0.5 M H_2SO_4, followed by the sequential addition of ferrous sulfate and hydrogen peroxide. The mixture was stirred on a mechanical shaker at 150 rpm for 30 minutes to initiate and sustain the Fenton reaction. Chemical oxygen demand (COD) was determined using the closed reflux method, as specified in standard procedures for water analysis (1999). Decolourization Efficiency (%) was calculated using;

$$\text{Decolourization Efficiency (\%)} = \frac{C_i - C_f}{C_i} \text{ X } 100 \qquad (2)$$

Where C_i is the initial concentration of dye (mg/L) and C_f is the final concentration of dye at reaction time (min).

➢ *Kinetics Models*

Kinetic models are essential for evaluating the reaction rates of chemical oxidation or adsorption processes and for identifying potential rate-limiting steps within the system (Madrakian *et al.*, 2012). In the context of chemical oxidation, commonly applied kinetic models include the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models. The pseudo-first-order kinetic model, originally introduced by Lagergren, was developed to describe the adsorption of solutes from liquid solutions onto solid surfaces. This model, often referred to as Lagergren's pseudo-first-order equation, has been widely employed to characterize adsorption kinetics in heterogeneous systems (Gurdag *et al.*, 2009).

$$\frac{dqt}{dt} = k_1 (C_e - C_t) \qquad (3)$$

Where k_1 is the pseudo first-order rate constant for the chemical oxidation process (min $^{-1}$), C_e and C_t are the equilibrium constant and equilibrium constant at every time t (min) respectively. After integration of this kinetic expression for the initial condition of C_t equal to 0, when time (t) approaches 0 yields

$$\text{Ln}(C_e/C_e - C_t) = k_1 t \qquad (4)$$

$\text{Log } (C_e - C_t) = \log C_t - \underline{k_1}t$

2.303

The linearize form gives: $\ln(C_e - C_t) = \ln C_e - k_1 t$ (5)

The plot of log (C_e-C_t) Vs t gives a straight line, and pseudo first-order rate constant k_1 can be calculated from the slope of that line.

➢ *Pseudo-Second-Order Kinetic Model*

In addition to the pseudo-first-order model, the kinetic behavior of the dye degradation process was also evaluated

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using the pseudo-second-order model proposed by Ho. The same experimental data employed for the pseudo-first-order analysis were applied here to determine the suitability of this alternative model. This approach helps assess the best fit for the kinetic behavior of the system. The pseudo-second-order model can be expressed in its linearized form as follows:

$$\frac{d_{qt}}{dt}= k_2(C_e-C_t)^2 \qquad (6)$$

Where k_2 is the rate constant of the pseudo second-order

(C_e-C_t) is the driving on rearrangement we get $\frac{d_{qt}}{C_e-C_t}=k_2dt$ (7)

By integrating the above equation with the boundary conditions of $q_t=0$ at $t=0$ and $q_t=q_t$ and $t=t$ we get

$$\frac{1}{(C_e=C_t)} = \frac{1}{C_e}+ k_2t \qquad (8)$$

The equation is further reduce to

$$\frac{t}{C_t}=\frac{1}{kC_e^2}+\frac{1\,t}{C_e} \qquad (9)$$

Where C_e is the concentration constant and C_t is the concentration constant at time t. t/Ct is plotted against t yield a linear relationship.

- *Thermodynamics Studies*

To gain a deeper understanding of the influence of temperature on the Fenton oxidation of dyes, key thermodynamic parameters—including Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS)—were evaluated. The values of ΔH and ΔS were calculated from the slope and intercept, respectively, of the linear plot of ln Kc versus 1/T, based on the following thermodynamic equation:

$$\ln K_c = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \qquad (10)$$

These values could be used to compute ΔG from the Gibb's relation,

$\Delta G= \Delta H-T\Delta S$

Where R is the universal gas constant (8.314 J/mol/K), T is the temperature (Kelvin) and K is the distribution coefficient.

III. RESULTS AND DISCUSSION

- *Influence of Initial Dye Concentration on Degradation Efficiency*

The impact of varying initial dye concentrations on the decolourization of Reactive Black 5 (RB5) and Methylene Blue (MB) using the Fenton process was investigated, with concentrations ranging from 50 to 300 mg/L, as illustrated in Figures 1a and 1b. The findings indicate that decolourization efficiency increases with rising dye concentration up to an optimal point, beyond which further increases result in a decline in removal efficiency. Specifically, concentrations exceeding 200 mg/L for RB5 and 150 mg/L for MB led to reduced decolourization, likely due to the saturation of hydroxyl radical capacity, limiting further oxidation. At higher dye concentrations, the generation of hydroxyl radicals (.OH) remains constant and does not scale proportionally with the increased dye molecules, thus reducing overall degradation performance (Sun *et al.*, 2007; Lucas & Peres, 2006).

For Methylene Blue, optimal decolourization of 99.28% was achieved at 150 mg/L dye concentration under conditions of 500 mg/L H_2O_2 and 50 mg/L $FeSO_4$. In the case of Reactive Black 5, a maximum removal efficiency of 99.20% was recorded at 200 mg/L using 300 mg/L H_2O_2 and 30 mg/L $FeSO_4$. These observations are consistent with the results reported by Argun and Karatas (2010), Barmani, Maleki, and Ghahramani (2013), and Haritash, Deepika, and Verma (2016).

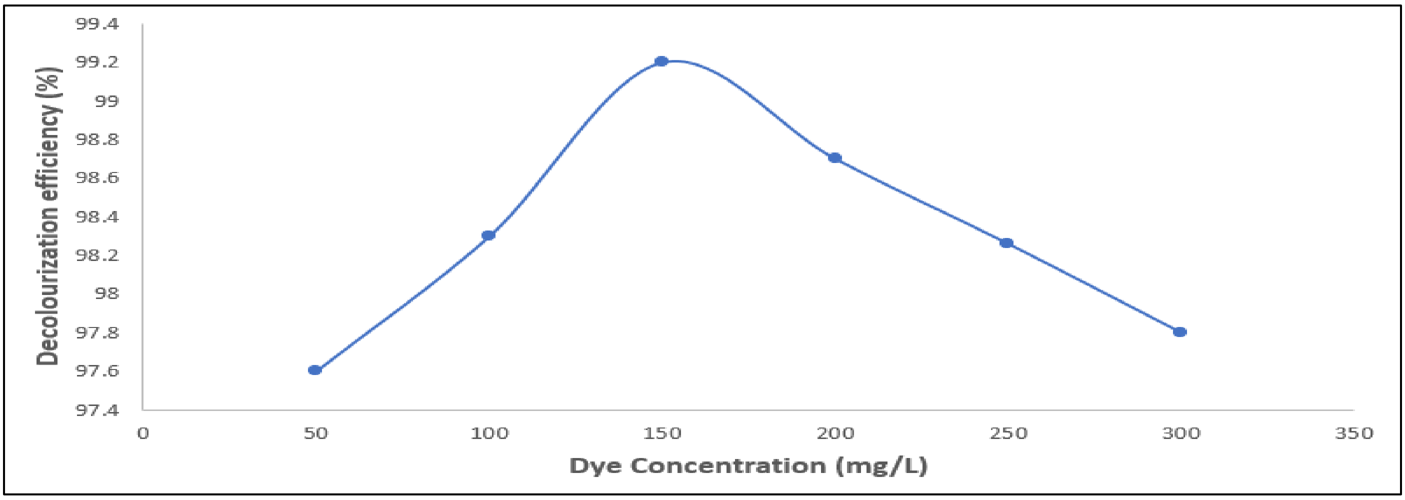

Fig 1a Effect of Initial Dye Concentration on Methylene Blue Decolourization. Experimental Conditions: H_2O_2 = 500 mg/L; $FeSO_4$ = 50 mg/L; pH = 3.

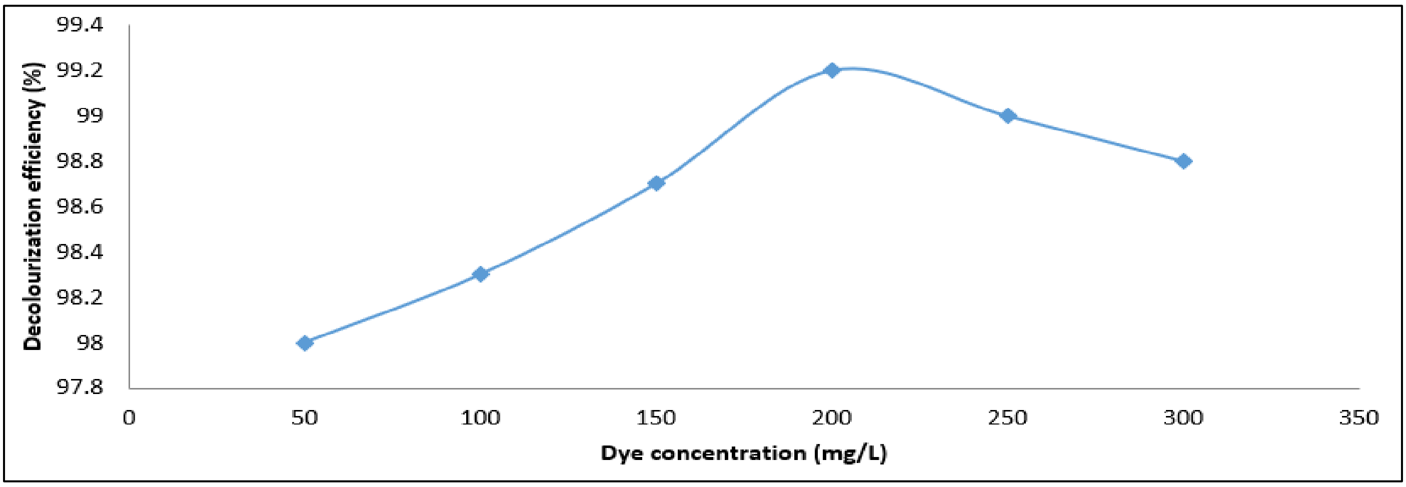

Fig 1b Effect of Initial Dye Concentration on Decolourization of Reactive Black 5. Experimental Conditions: H_2O_2 = 300 mg/L; $FeSO_4$ = 30 mg/L; pH = 3

- *Effect of Hydrogen Peroxide Concentration on Dye Decolourization*

The influence of hydrogen peroxide (H_2O_2) concentration on the decolourization of Methylene Blue (MB) and Reactive Black 5 (RB5) using the Fenton process was examined, with the results illustrated in Figures 2a and 2b. Experiments were conducted at an acidic pH of 3, maintaining fixed concentrations of $FeSO_4$ at 50 mg/L for MB and 30 mg/L for RB5, and dye concentrations of 150 mg/L and 200 mg/L, respectively. The concentration of H_2O_2 was varied between 100 and 600 mg/L.

As presented in Figures 2a and 2b, an increase in H_2O_2 concentration from 100 to 500 mg/L resulted in enhanced decolourization of MB from 95.59% to 99.32% after 60 minutes of treatment. Similarly, increasing H_2O_2 from 100 to 300 mg/L improved the decolourization of RB5 from 97.8% to 99.21%. These findings are consistent with previous studies (Fu, Wang, & Tang, 2010; Elmorsi, 2010), which indicate that a moderate increase in H_2O_2 dosage generally promotes pollutant degradation. However, exceeding the optimal H_2O_2 concentration is not advisable, as reported by Lin and Lo (1997).

Further increases in H_2O_2 concentration beyond 500 mg/L for MB and 300 mg/L for RB5 did not yield notable improvements in decolourization efficiency. This decline in efficiency at higher H_2O_2 concentrations is attributed to the scavenging effect of excess H_2O_2 on hydroxyl radicals (.OH), which impairs the oxidative capacity of the system. Such behavior is characteristic of Fenton-based processes, wherein excess H_2O_2 reacts with .OH radicals, forming less reactive species such as HO_2• and H_2O_2 itself, as shown in Equations 11 to 13:

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO^{\cdot}_2 \qquad (11)$$

$$HO^{\cdot}_2 + {}^{\cdot}OH \rightarrow H_2O + O_2 \qquad (12)$$

$$OH + {}^{\cdot}OH \rightarrow H_2O_2 \qquad (13)$$

Based on these observations, optimal H_2O_2 concentrations for maximum dye decolourization were identified as 500 mg/L for Methylene Blue and 300 mg/L for Reactive Black 5. These results align with the findings reported by Sun et al. (2007), Bahmani, Maleki, and Ghahramani (2013), Haritash, Deepika, and Verma (2016), and Khan *et al.* (2019).

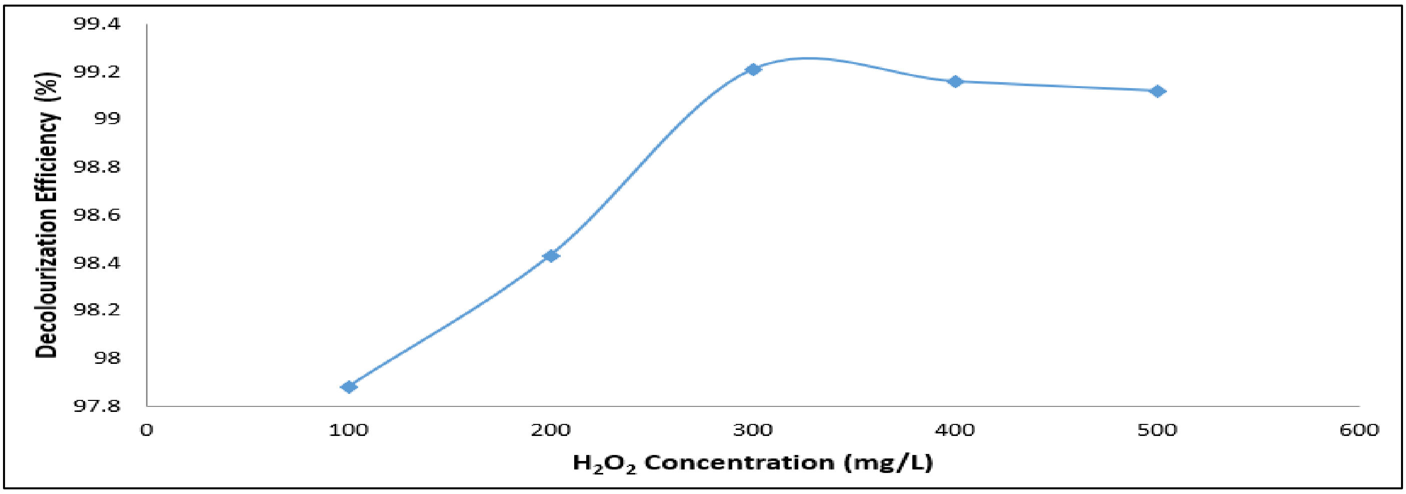

Fig 2a Effect of H_2O_2 Concentration on Decolourization of Reactive Black 5.
Experimental Conditions: RB5 = 200 mg/L; $FeSO_4$ = 50 mg/L; pH = 3

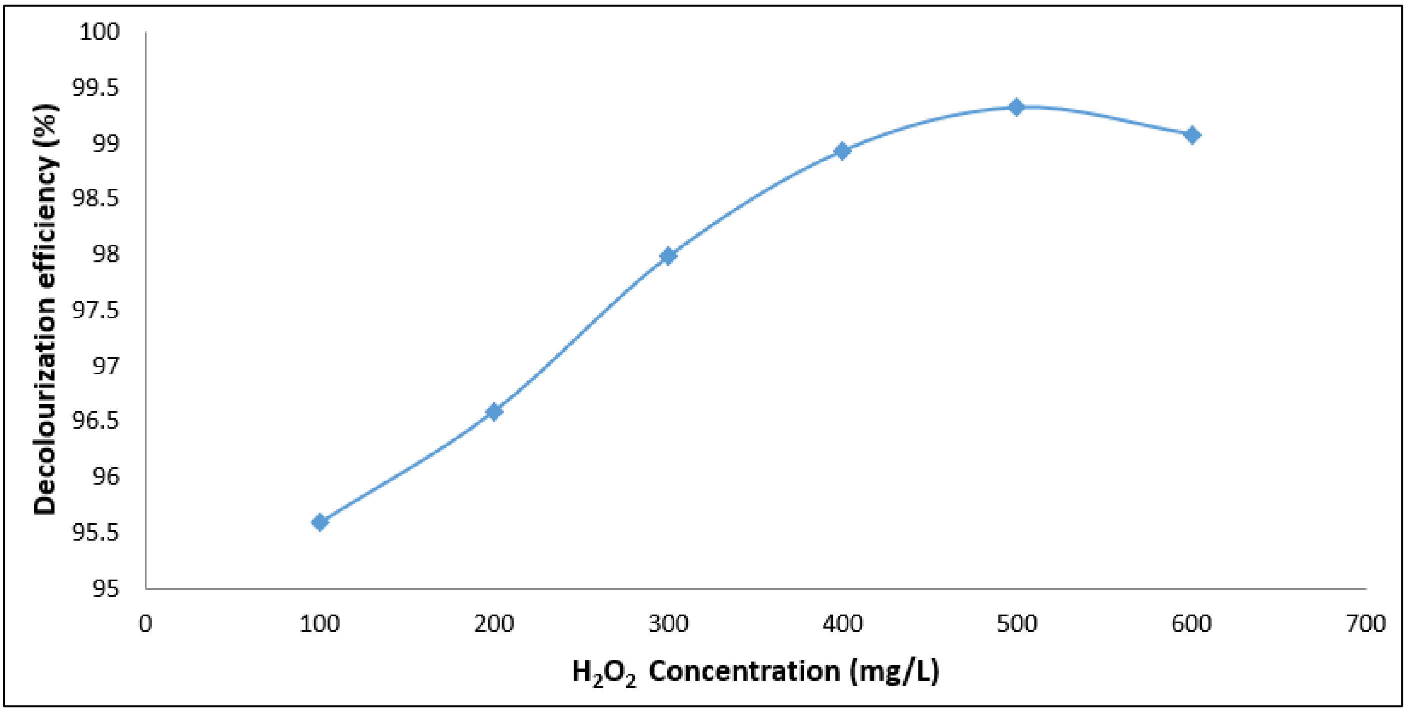

Fig 2b Effect of H_2O_2 Concentration on Decolourization of Methylene Blue.
Experimental Conditions: Methylene Blue = 150 mg/L; $FeSO_4$ = 50 mg/L; pH = 3

- *Effect of Ferrous Sulphate Concentration*

The efficiency of dye degradation through the Fenton process is significantly influenced by the concentration of ferrous ions (Fe^{2+}), which serve as catalysts in the decomposition of hydrogen peroxide, leading to the formation of hydroxyl radicals (•OH) responsible for the breakdown of organic pollutants. To evaluate this effect, the concentration of Fe^{2+} was varied from 10 to 100 mg/L, while keeping the hydrogen peroxide concentration, pH, and dye concentration constant (500 mg/L and 300 mg/L H_2O_2, 150 mg/L and 200 mg/L dye for Methylene Blue and Reactive Black 5, respectively).

The findings indicated that the decolourization efficiency improved from 97.8% to 99.3% as the Fe^{2+} concentration increased from 10 to 50 mg/L within 30 minutes of treatment. However, further increases in Fe^{2+} concentration led to a decline in colour removal efficiency. This trend can be attributed to the stoichiometric imbalance between Fe^{2+} and H_2O_2—while a higher amount of ferrous ions enhances •OH radical generation, the fixed amount of hydrogen peroxide becomes the limiting reagent beyond a certain threshold. Since Fe^{2+} acts solely as a catalyst in the Fenton reaction, an excess of ferrous ions may accelerate H_2O_2 consumption until it is depleted. Once all available hydrogen peroxide is used up, additional ferrous ions no longer contribute effectively to the reaction and may accumulate without playing any catalytic role.

This phenomenon aligns with observations by Kusic (2006) and Rathi (2003), who noted that increasing the Fe^{2+} concentration improves degradation efficiency only up to an optimal point. Beyond that, excess Fe^{2+} can react with •OH radicals or undergo redox reactions that reduce the overall efficiency of the process, as also reported by Hsueh *et al.* (2005).

$$Fe^{2+}+{}^{\circ}OH \rightarrow OH^{\circ}+Fe^{3+} \quad (14)$$

$$H_2O_2+{}^{\circ}OH \rightarrow HO_2{}^{\circ}+H_2O^{+} \quad (15)$$

Ferric ions (Fe^{3+}), generated during the Fenton reaction, may further interact with hydrogen peroxide and hydroperoxyl radicals to regenerate Fe^{2+} in solution. However, this regeneration can also lead to a reduction in overall dye removal efficiency (Benitez *et al.,* 2001). Experimental results demonstrated that the highest decolourization efficiency was achieved at Fe^{2+} concentrations of 50 mg/L for Methylene Blue and 30 mg/L for Reactive Black 5.

Accordingly, it was determined that optimal conditions for maximum decolourization (99.1%) of Methylene Blue included 50 mg/L of $FeSO_4$ and 500 mg/L of H_2O_2 at a solution pH of 3. Similarly, Reactive Black 5 achieved a decolourization rate of 99.4% under conditions of 30 mg/L $FeSO_4$ and 300 mg/L H_2O_2 at the same pH. These results corresponded to optimal dye:H_2O_2:$FeSO_4$ mass ratios (w/w/w) of 1:3.3:0.1 for Methylene Blue and 1:1.5:0.1 for Reactive Black 5.

Comparable findings were reported by Bahmani, Maleki, and Ghahramani (2013), who observed 97% decolourization of Reactive Black 5 at a dye:H_2O_2:Fe^{2+} ratio of 1:1.2:0.16 (w/w/w). In another study by Lodha and Chaudhari (2007), similar degradation efficiencies (97–98%) were achieved for dyes including RB5, RB13, and AO7 using a dye:H_2O_2:Fe^{2+} ratio of 1:1:0.3.

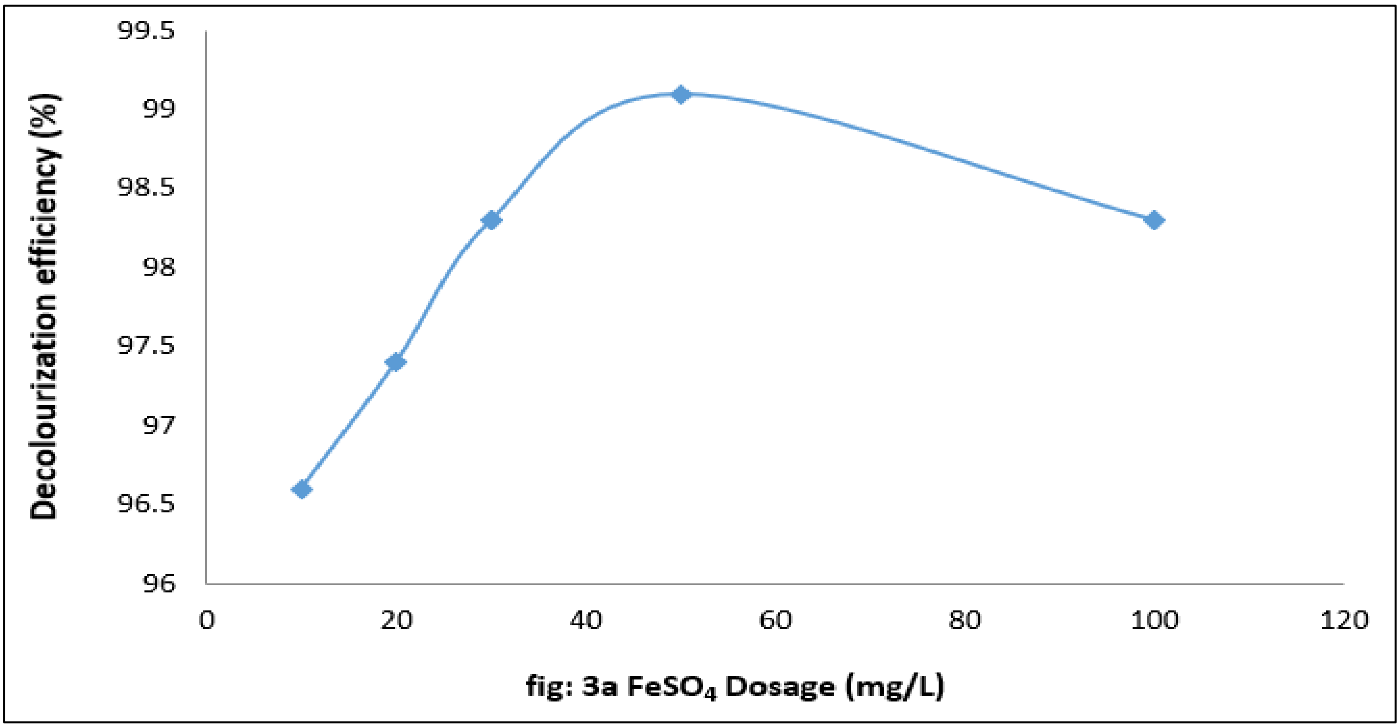

Fig 3a Effect of $FeSO_4$ on Decolourization of Methylene Blue.
Experimental Conditions: Methylene Blue = 150 mg/L; H_2O_2 = 500 mg/L; pH = 3

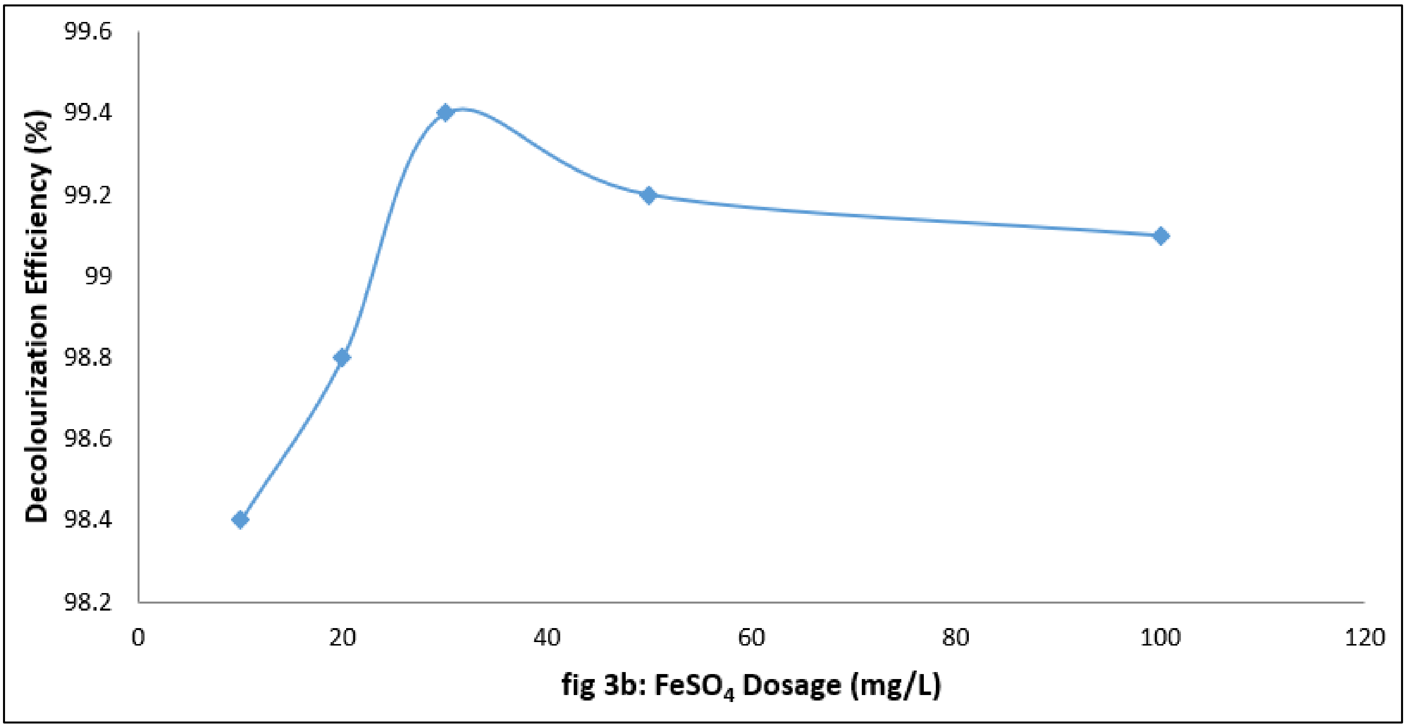

Fig 3b Effect of $FeSO_4$ on Decolourization of Reactive Black 5.
Experimental Conditions: Reactive Black = 200 mg/L; H_2O_2 = 300 mg/L; pH = 3

- *Influence of Reaction Time on Dye Decolourization*

The impact of contact time on the decolourization efficiency of Reactive Black 5 and Methylene Blue using the Fenton oxidation process was investigated, with results illustrated in Figures 4a and 4b. The study assessed reaction durations ranging from 5 to 60 minutes. A rapid colour removal was observed during the initial phase of the reaction for both dyes. Within the first 5 minutes, decolourization efficiencies of 93.11% for Methylene Blue and 98.25% for Reactive Black 5 were recorded. These values further increased to 99.34% and 99.20%, respectively, after 25 minutes of treatment. Beyond this time, no significant increase in decolourization was observed, indicating that the process had reached completion at 25 minutes for Methylene Blue and 20 minutes for Reactive Black 5.

Similar observations were reported by Malik and Saha (2003), who found that approximately 70% of dye degradation occurred within the first minute, followed by a gradual increase, reaching nearly 97% after 30 minutes. Comparable findings were also noted by Rodrigues and Boaventura (2009) and Hsing, Chiang, and Chang (2007), who achieved high decolourization efficiency in under 20 minutes.

The Fenton reaction is typically characterized by a two-stage mechanism (Ramirez, 2009). In the initial phase, referred to as the Fe^{2+}/H_2O_2 stage, ferrous ions rapidly react with hydrogen peroxide to generate hydroxyl radicals, which aggressively attack the dye molecules. This results in a swift decline in colour concentration. In the subsequent Fe^{3+}/H_2O_2 phase, the rate of degradation slows down due to the limited regeneration of Fe^{2+} from Fe^{3+}, leading to a reduced availability of hydroxyl radicals and thus a slower reaction rate.

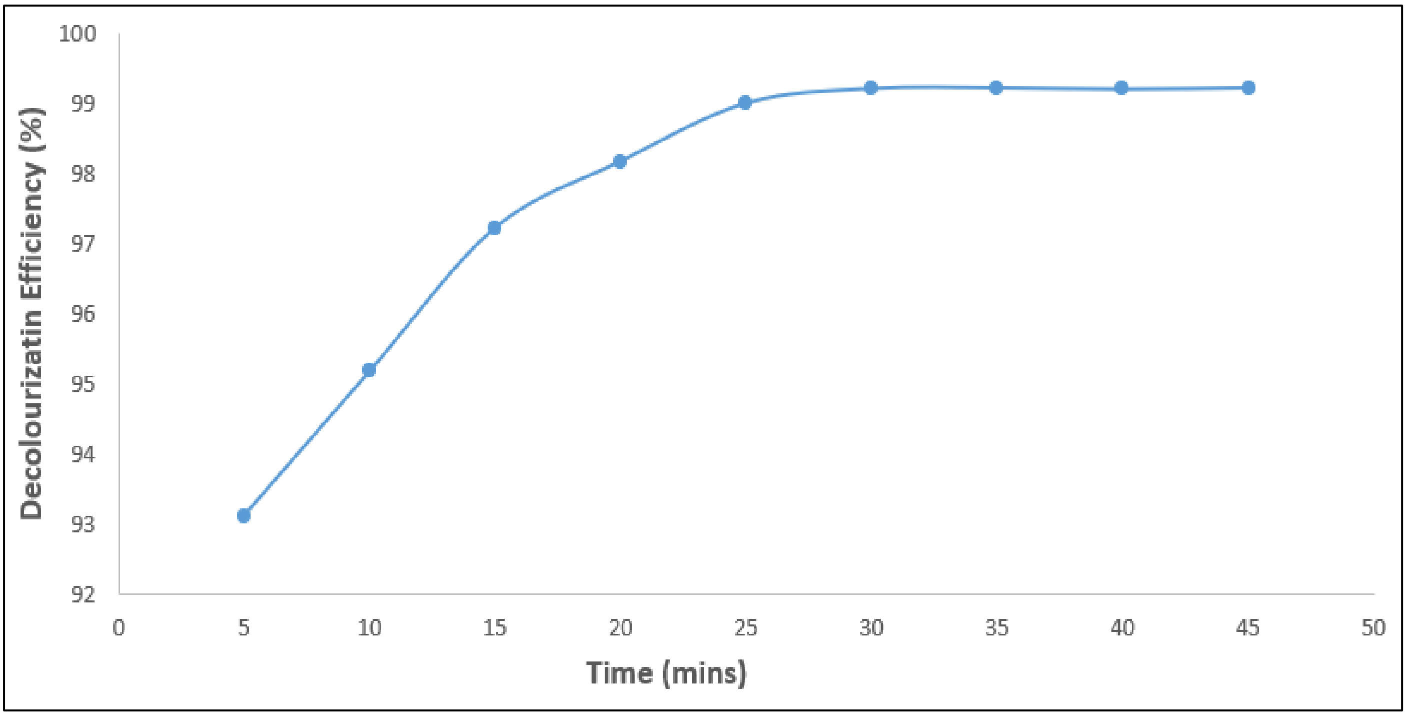

Fig 4a Effect of Time on Decolourization of Methylene Blue.
Experimental Conditions: Methylene Blue = 150 mg/L; H_2O_2 = 500 mg/L; $FeSO_4$= 50 mg/L; pH = 3

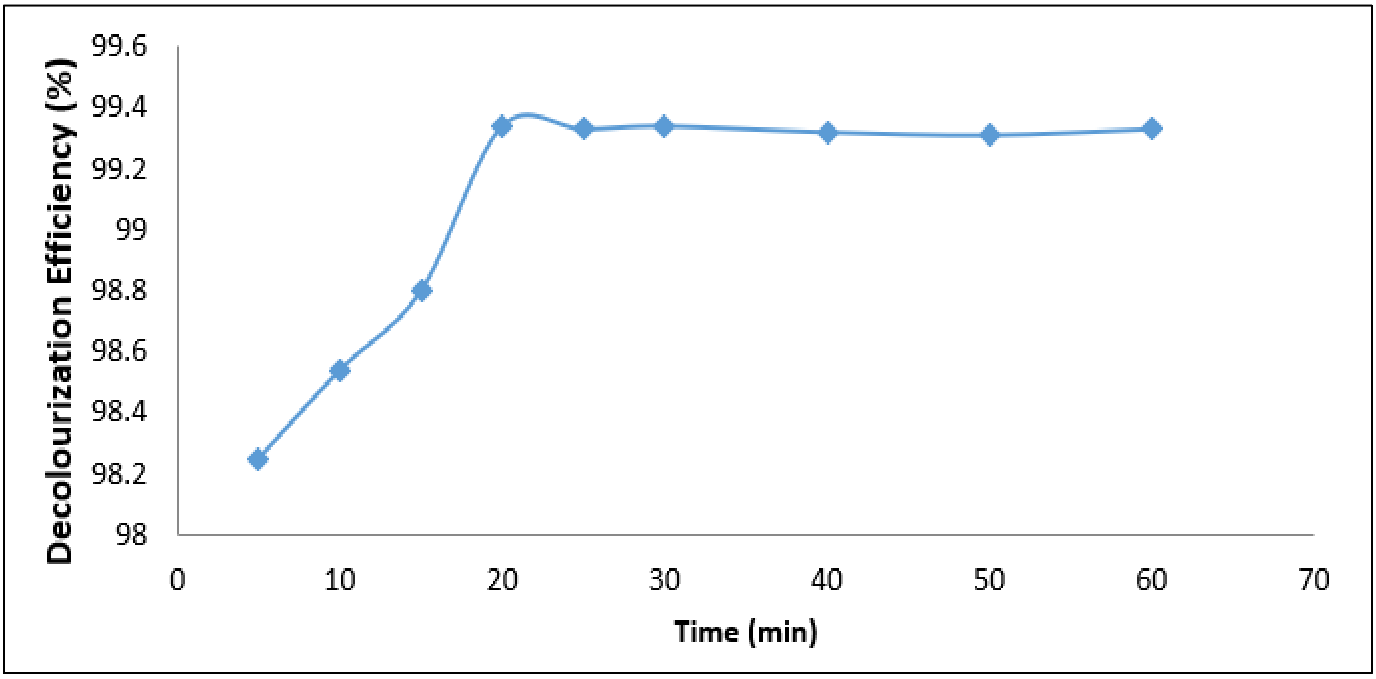

Fig 4b Effect of Time on Decolourization of Reactive Black 5.
Experimental Conditions: Reactive Black 5= 200 mg/L; H_2O_2 = 300 mg/L; $FeSO_4$= 30 mg/L; pH = 3

➢ *Effect of pH on Dye Decolourization*

The influence of initial pH on the Fenton-mediated decolourization of Methylene Blue and Reactive Black 5 was assessed, and the findings are presented in Figures 3.6a and 3.6b. pH plays a critical role in determining the efficiency of the Fenton oxidation process. In this study, the reactions were conducted for 30 minutes under controlled conditions, with fixed concentrations of Fe^{2+} (50 mg/L for Methylene Blue and 30 mg/L for Reactive Black 5) and H_2O_2 (500 mg/L and 300 mg/L, respectively).

As illustrated in the figures, the decolourization efficiency was highest at an acidic pH and declined as the pH increased. At pH 3, the removal efficiencies were 99.16% for Methylene Blue and 99.30% for Reactive Black 5. However, at neutral pH (pH 7), the efficiencies dropped substantially to 43.6% and 46.5%, respectively. These results clearly identify pH 3 as the optimal condition for effective dye removal in this system.

These findings are consistent with previous research. For instance, Sun *et al.* (2007) reported 98.83% decolourization of Acid Black 1 under similar acidic conditions within 30 minutes. Lucas and Peres (2006) also identified pH 3 as the optimal value for the Fenton oxidation of Reactive Black 5. The observed decline in decolourization efficiency at higher pH values may be attributed to a reduction in the oxidation potential of hydroxyl radicals (·OH) in alkaline environments, as discussed by Sun *et al.* (2007). Argun and Karatas (2010) also observed 99% removal efficiency for Reactive Black 5 at pH 3, while Kuo (1992) reported 97% dye removal under similar conditions. In support, Malik and Saha (2003) and Meric, Kaptan, and Olmez (2004) demonstrated that maximum colour removal—often exceeding 99%—is typically achieved within the pH range of 3 to 3.5. 99% of colour removal was possible in the pH range of 3–3.5.

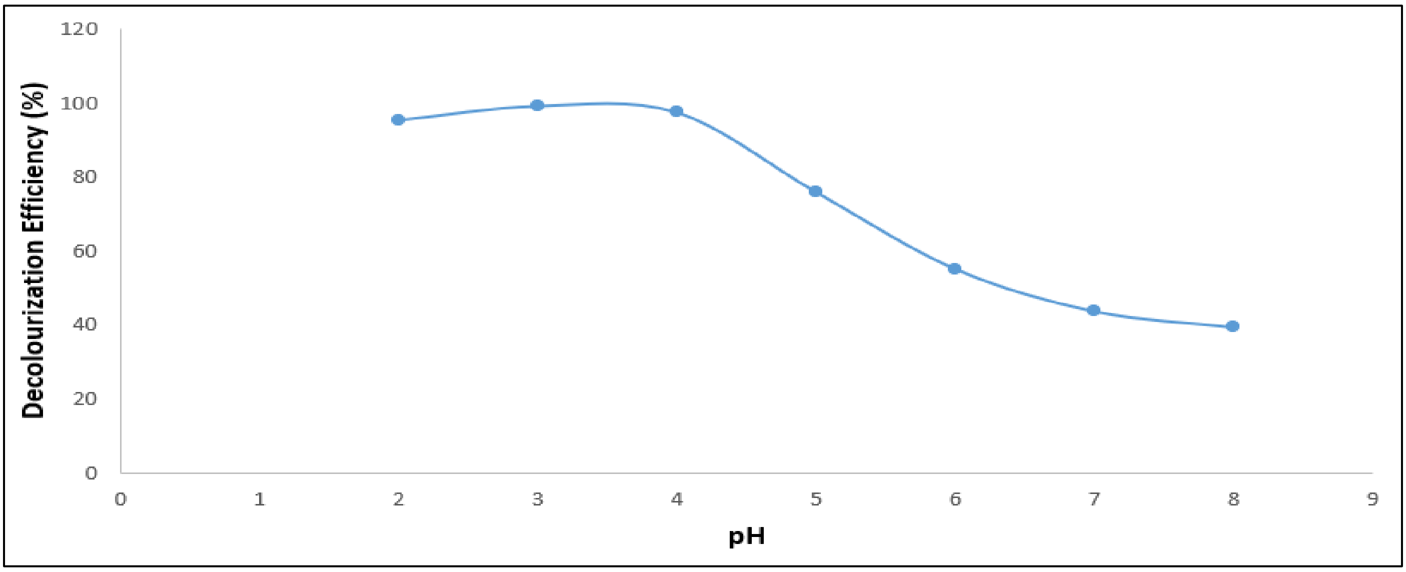

Fig 5a Effect of pH on Decolourization of Methylene Blue.
Experimental Conditions: Methylene Blue= 150 mg/L; H_2O_2 = 500 mg/L; $FeSO_4$= 50 mg/L

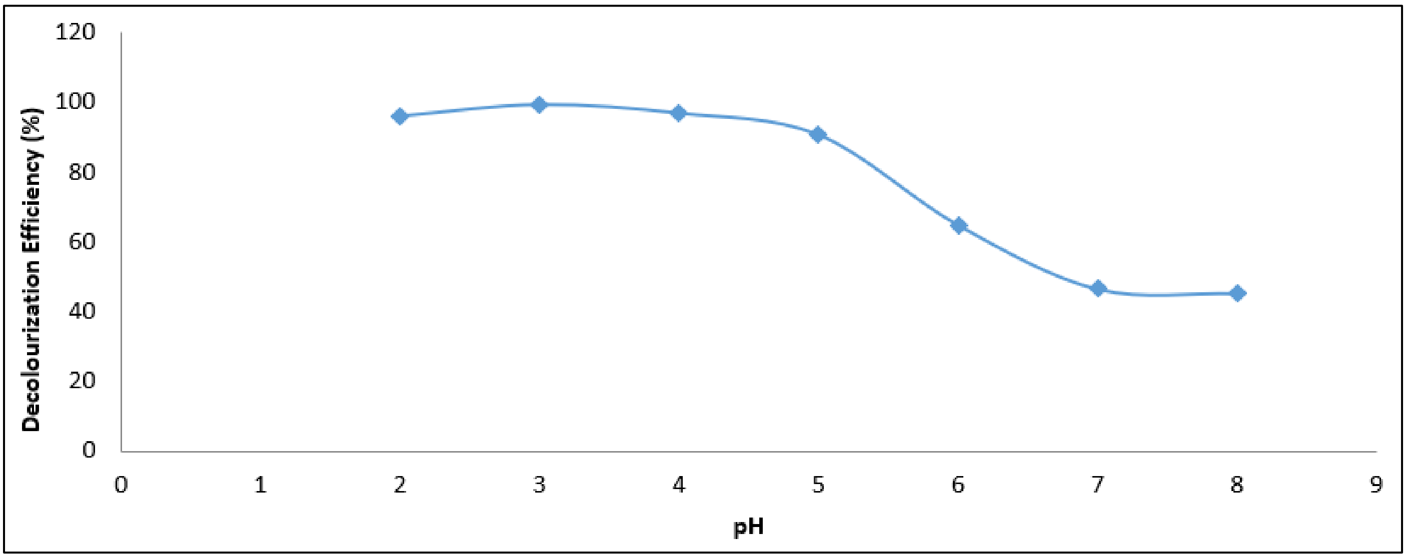

Fig 5b Effect of pH on Decolourization of Reactive Black 5.
Experimental Conditions: Reactive Black 5= 200 mg/L; H_2O_2 = 300 mg/L; $FeSO_4$= 30 mg/L

- *Effect of Temperature on Dye Decolourization*

An increase in temperature was found to significantly enhance the decolourization efficiency of both Methylene Blue and Reactive Black 5 dyes using the Fenton process. As the temperature rose from 20 °C to 40 °C, the decolourization efficiency improved from 97.40% to 99.47% for Reactive Black 5 within 20 minutes, and from 98.02% to 99.46% for Methylene Blue within 25 minutes. This improvement is attributed to the acceleration of redox reactions at elevated temperatures, which enhances the production of hydroxyl radicals (·OH) responsible for dye degradation.

Optimal removal efficiencies were recorded at 40 °C, achieving 99.42% for Methylene Blue and 99.47% for Reactive Black 5 after 30 minutes of treatment. These findings align with the observations of Gulkaya (2006), who noted that while higher temperatures tend to increase ·OH generation, temperatures exceeding 60 °C may trigger the self-decomposition of hydrogen peroxide, thereby reducing the availability of ·OH and ultimately decreasing reaction efficiency.

Further studies support this trend, indicating that temperature elevation positively influences dye degradation (Emami, 2010; Sun *et al.*, 2009). Moreover, higher temperatures contribute to shorter reaction times required for effective decolourization. Similar conclusions were drawn by Kavitha and Palanivelu (2005) as well as Lucas and Peres (2009), who identified the optimal operating temperature for wastewater treatment to lie within the 30–40 °C range. Wu *et al.* (2010), however, reported a slightly higher optimum at 45 °C.

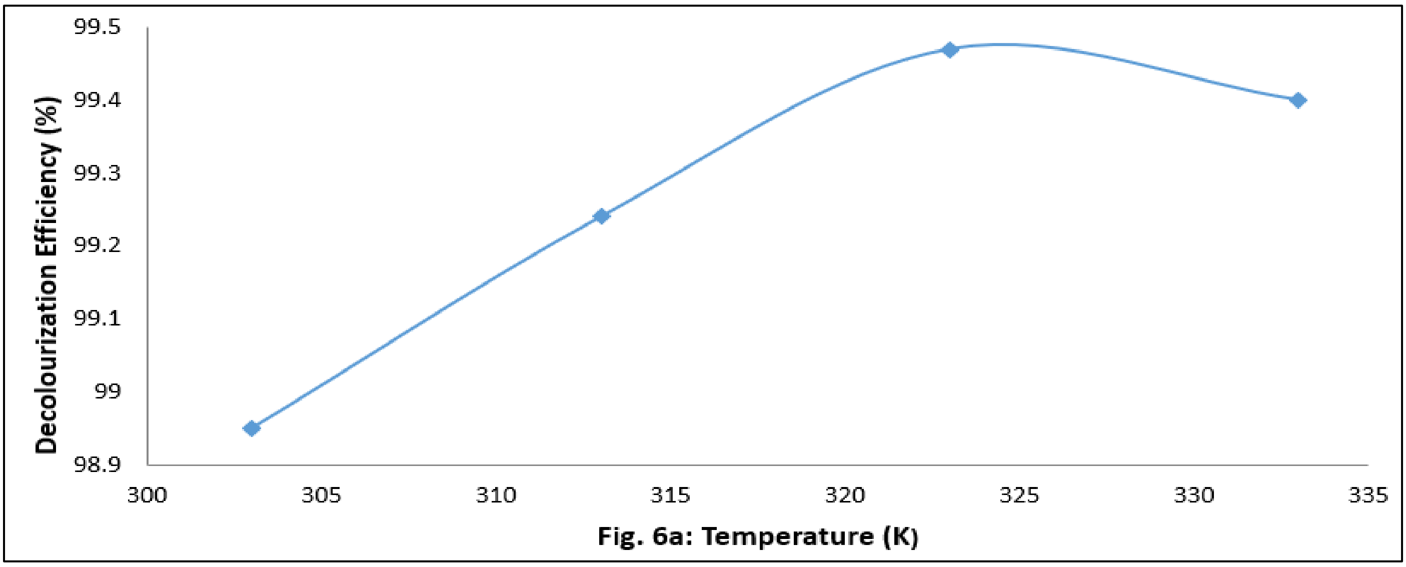

Fig 6a Effect of Temperature on Decolourization of Reactive Black 5.
Experimental Conditions: Reactive Black 5= 200 mg/L; H_2O_2 = 300 mg/L; $FeSO_4$= 30 mg/L; pH = 3

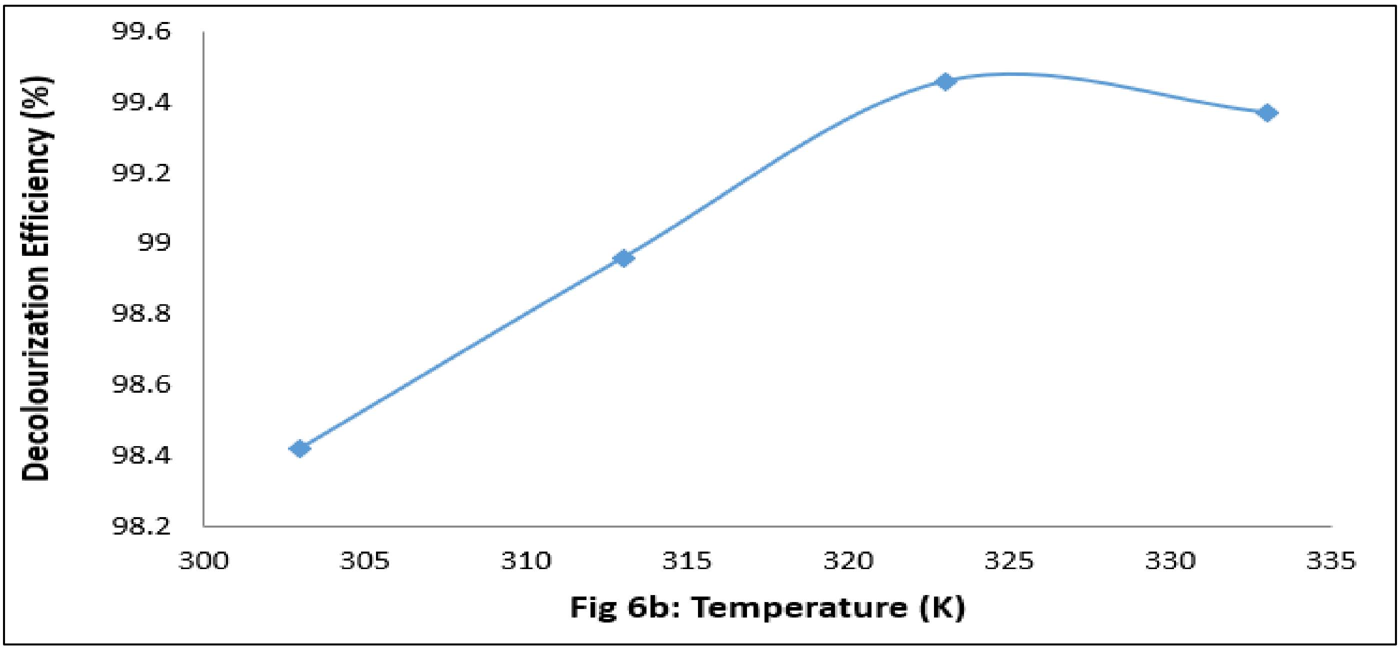

Fig 6b Effect of Temperature on Decolourization of Methylene Blue.
Experimental Conditions: Methylene Blue = 150 mg/L; H_2O_2 = 500 mg/L; $FeSO_4$= 50 mg/L; pH= 3.

- *Kinetic Models for Fenton Oxidation of RB5 and Methylene Blue*

The kinetics of the Fenton oxidation process were investigated using pseudo-first-order and pseudo-second-order kinetic models. These models were applied to describe the degradation behavior of Reactive Black 5 and Methylene Blue over time in the presence of the adsorbent. Graphical representations of the kinetic analyses are provided in Figures 3.8a and 3.8b. The pseudo-first-order model exhibited a poor fit to the experimental data, as indicated by relatively low correlation coefficients (R^2 values of 0.7692 for Methylene Blue and 0.4058 for Reactive Black 5). In contrast, the pseudo-second-order model provided a much better fit, demonstrating strong agreement with the experimental results, with R^2 values of 0.965 and 0.9882 for Methylene Blue and Reactive Black 5, respectively.

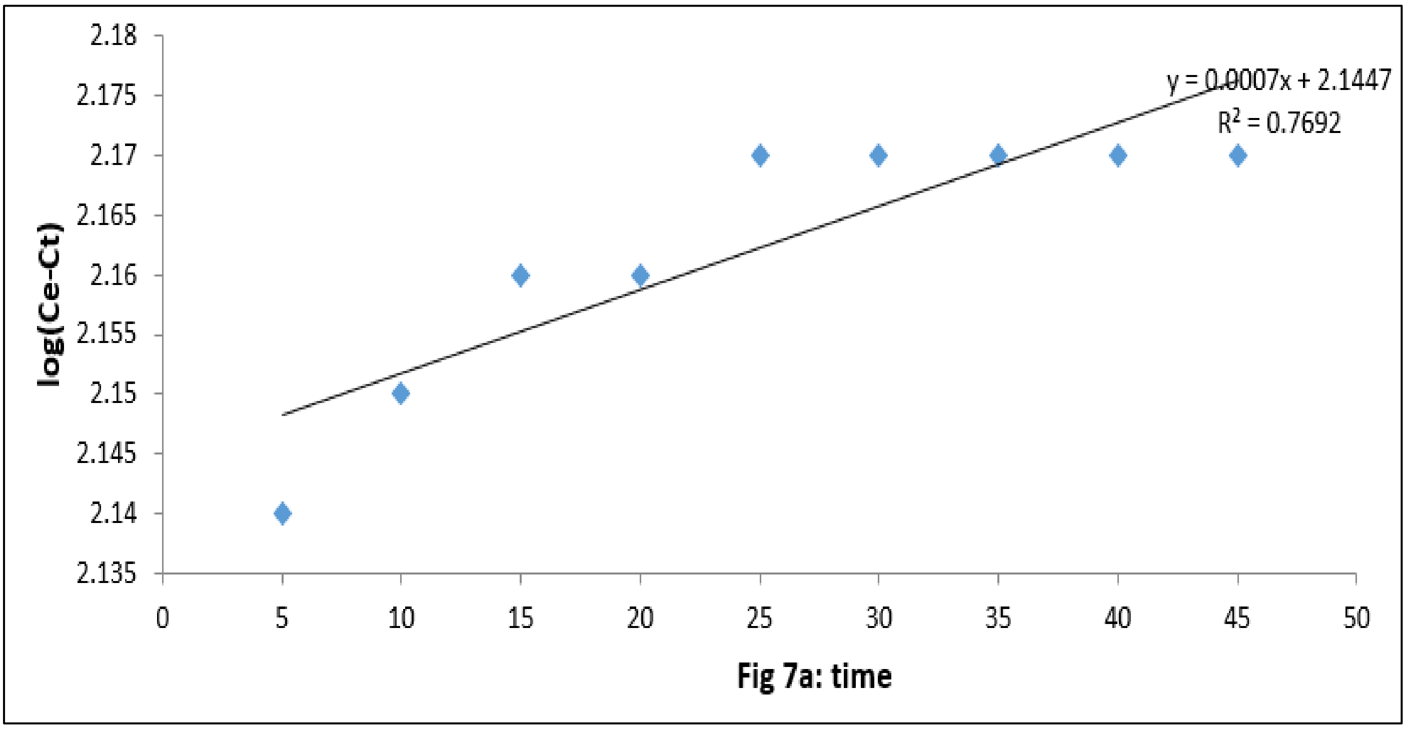

Fig 7a Pseudo First Order for Methylene Blue

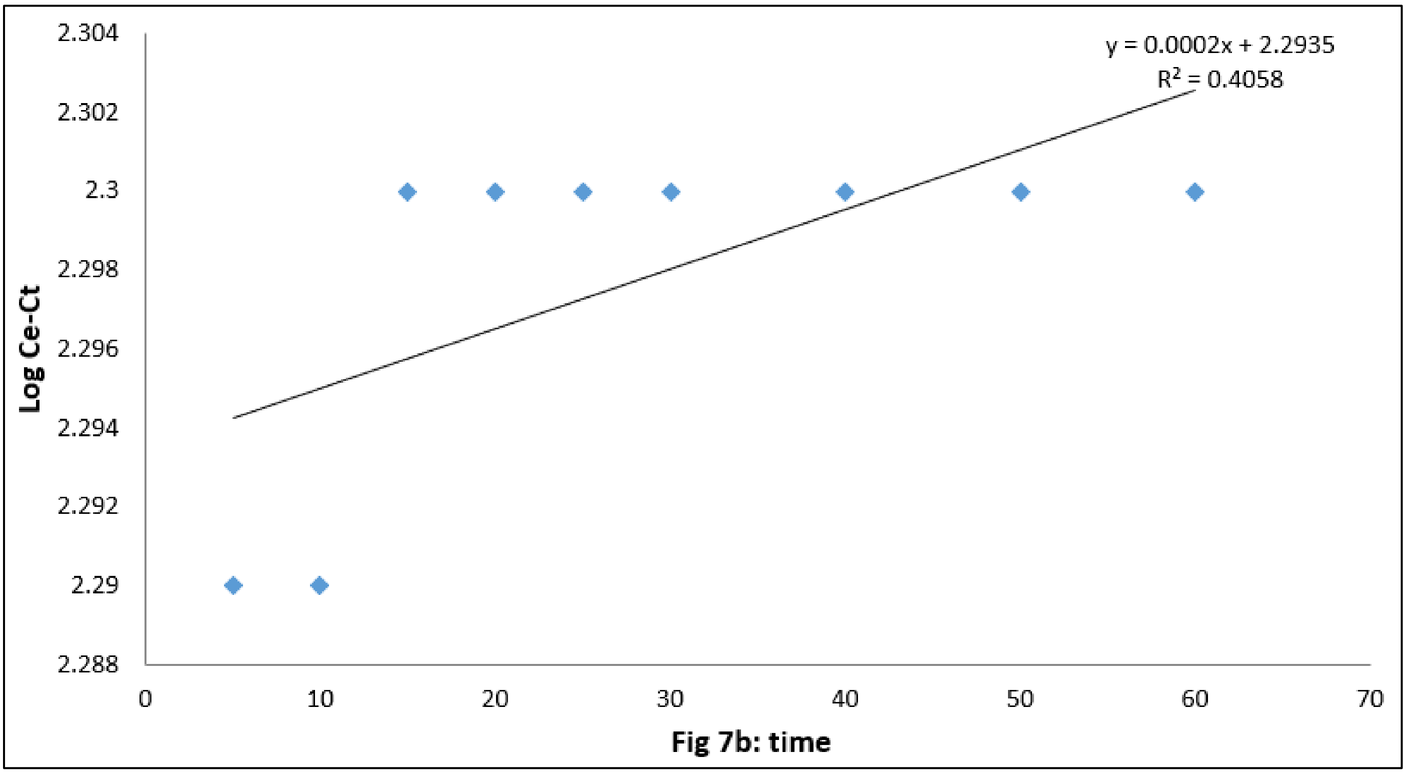

Fig 7b Pseudo First Order of Reactive Black 5

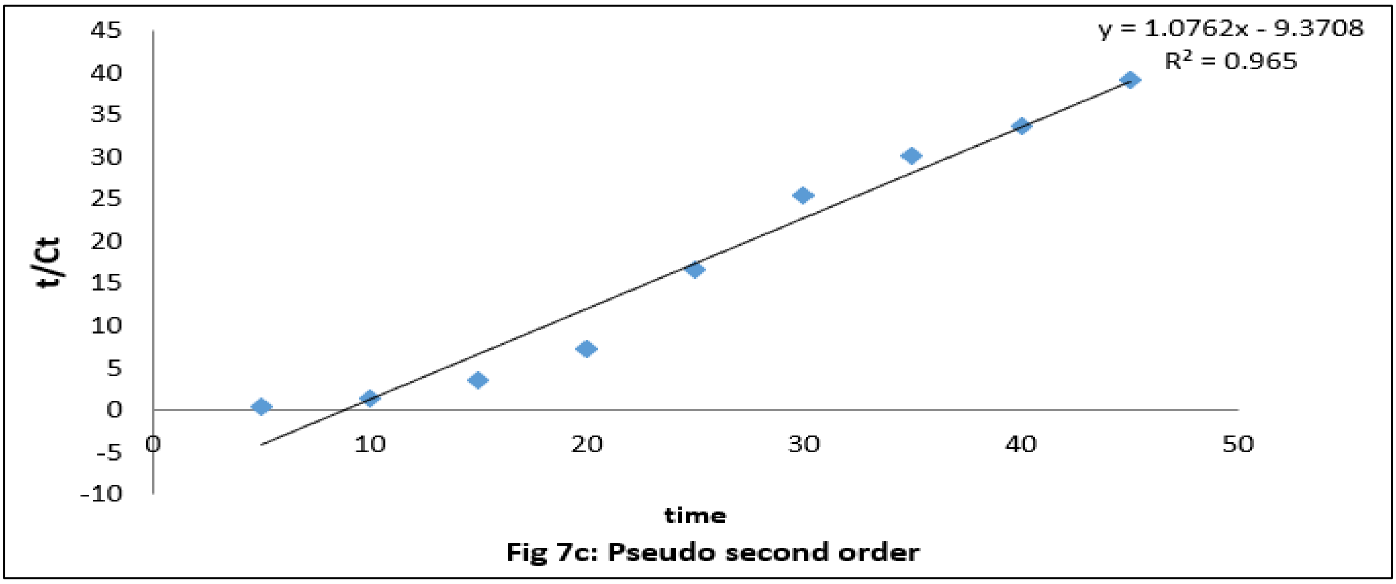

Fig 7c Pseudo Second Order for Methylene Blue

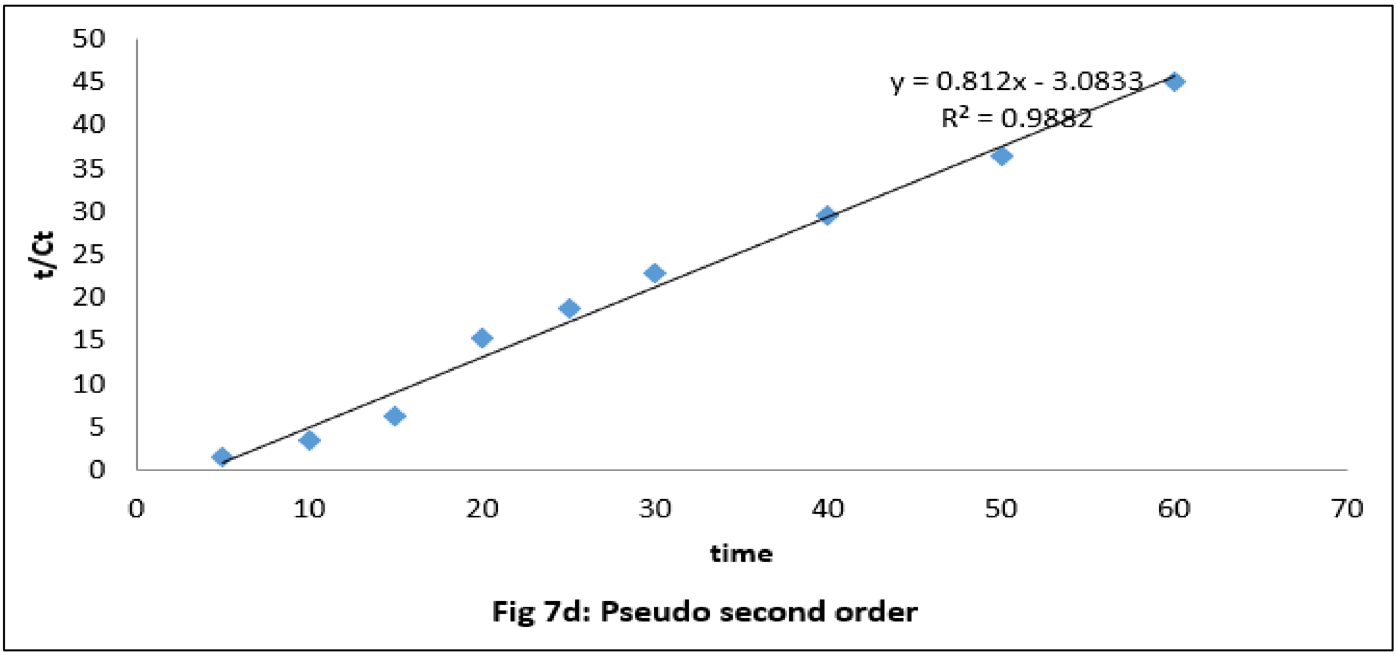

Fig 7d: Pseudo Second Order for Reactive Black 5

- *Thermodynamics of Reactive Black 5 and Methylene Blue using Fenton Oxidation*

The influence of temperature on the Fenton oxidation of Reactive Black 5 and Methylene Blue was analyzed using thermodynamic models to determine key thermodynamic parameters. These parameters—Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS)—were calculated to characterize the oxidation process. The values of ΔH and ΔS were derived from the slope and intercept, respectively, of the van't Hoff plots constructed by plotting lnK against 1/T. The corresponding thermodynamic parameters are presented in the table below. As shown in Table 1, the negative values of ΔG at various temperatures indicate that the oxidation process is thermodynamically spontaneous, although the spontaneity decreases with rising temperature. The positive ΔH value confirms that the reaction is endothermic in nature.

Table 1 Thermodynamic Parameters (ΔH, ΔS and ΔG) for the Fenton Oxidation of Methylene Blue and Reactive Black 5

	Methylene blue	**Reactive black 5**	**Methylene blue**		**Reactive black 5**	
Temperature (K)	**ΔG(KJ/mol)**	**ΔG(KJ/mol)**	**ΔH(KJ/mol)**	**ΔS(KJ/mol)**	**ΔH(KJ/mol)**	**ΔS(KJ/mol)**
293	-9.16	-10.85	28.93	0.13	18.45	0.10
303	-10.46	-11.85				
313	-11.76	-12.85				
323	-13.06	-13.85				

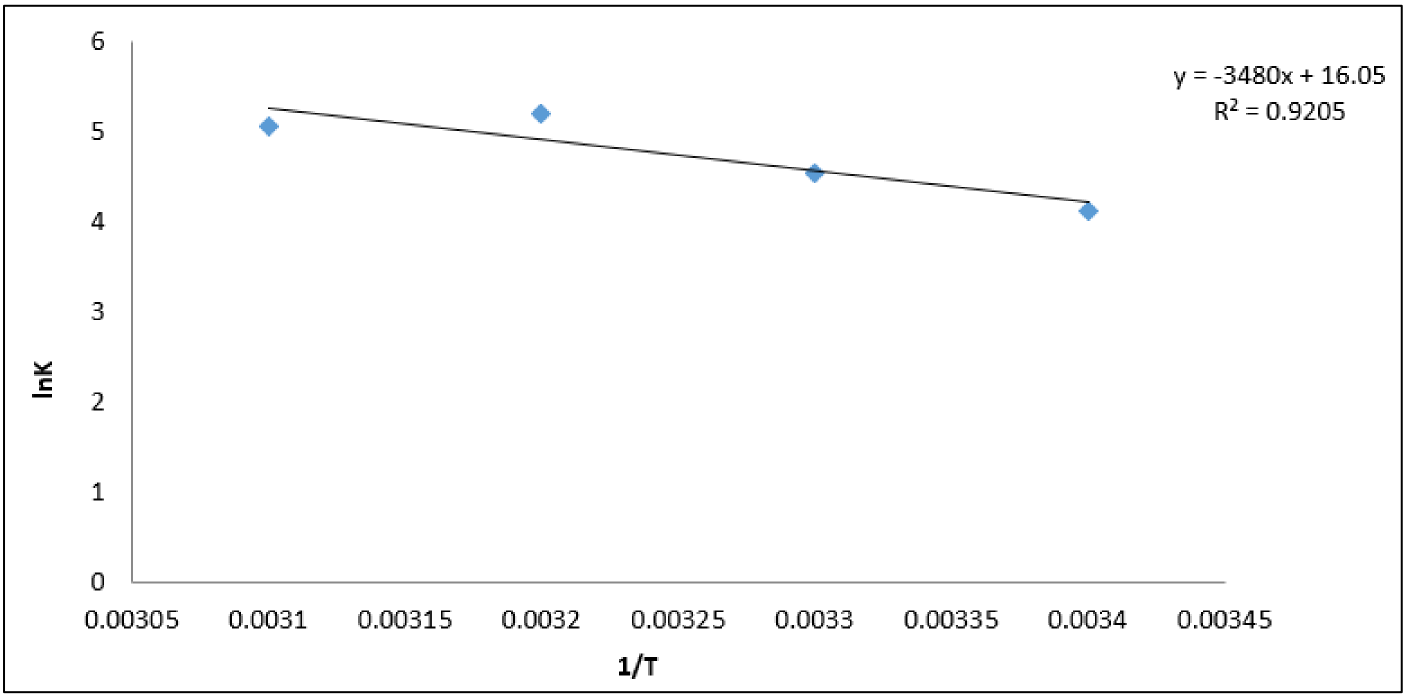

Fig 8a: Thermodynamics for Methylene blue

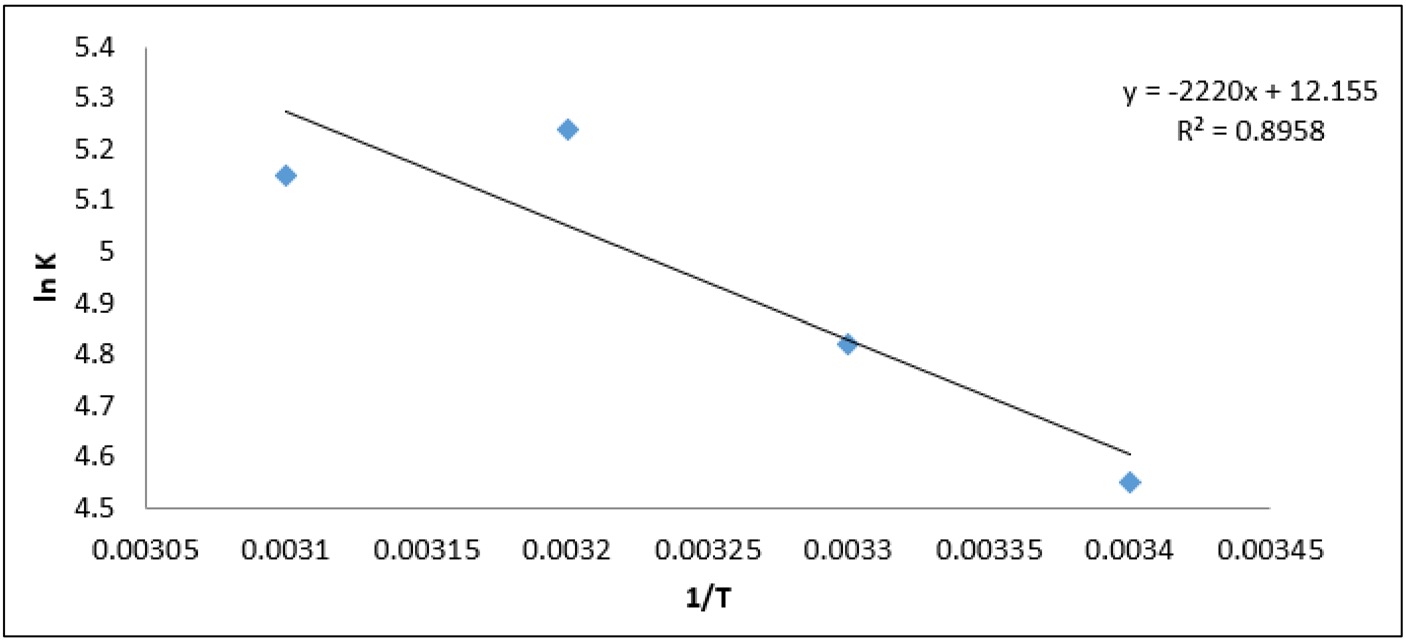

Fig 8b Thermodynamics for RB5

- *GC-MS Analysis Results*

In order to further analyse the degradation products of Reactive black 5 and methylene blue dyes by Fenton oxidation, GC-MS analysis was performed before and after Fenton oxidation and the results were shown in the Table 2-5 below.

GC-MS chromatogram of the Reactive Black 5 in aqueous solution before Fenton oxidation shows twenty eight (28) peaks indicating 28 chemical compounds while Methylene blue in aqueous solution shows eleven (11) peaks. The active principles with their retention time (RT), final time (FT), peak area, height (%) in reactive black 5 & Methylene blue before and after Fenton oxidation is presented in table below. It also shows the mass spectrum compounds.

On comparison with Reactive Black 5 after Fenton oxidation, only fourteen (14) peaks were obtained indicating the presence of 14 chemical compounds while Methylene blue after Fenton oxidation shows seven (7) peaks after Fenton oxidation. This shows that degradation has occurred after Fenton oxidation. The 14 peaks suggested that degradation as occurred compared to 28 peaks in Reactive Black 5 aqueous solution (before Fenton oxidation).

For RB5 and Methylene blue after degradation by Fenton oxidation, the chemical compounds include linear aliphatic alcohols compounds and Isosorbide (D-Glucitol). Linear aliphatic alcohols compounds includes 2-Propanol, 1-bromo- and 1, 2-cyclopentanedione, 3-methyl were identified in this study. Xie, Liub, and Yanga, (2018) also detected linear aliphatic alcohol such as 1,2,3-propanetriol after degradation by Fenton oxidation of Reactive black 5. The 1,3-Benzenediol, O-isobutyryl-O'-methoxyacetyl and 1, 2-Cyclopentanedione, 3-methyl identified in all samples can be attributed to the materials in the production of dyes. Also 2-Imidazolidinone, 1,3-dimethyl present in both Reactive black 5 samples (treated and untreated) is used in the variety of application including dyestuffs.

It was also observed from the results that toxic compounds such as methoxyacetic acid, 1, 4-Bis (trimethylsilyl)benzene, Isophthalic acid, allyl dodecyl ester, cis-1-(4-Isopropylphenyl)-3-(2-furyl) cyclopropane,1, 4-Bis (trimethylsilyl) benzene,9-Acetyl-S-octahydrophenanthrene and 3-Amino-2,6-dimethoxypyridine were absent from the Reactive black 5 after Fenton treatment.

In addition, toxic compounds in Methylene Blue aqueous solution such as 2,4,5,7-Tetramethyl-1,2,3,4-tetrahydropyrimido[3,4-a]indole, Cyclohexene, 3-butyl-3-methy l-1-trimethylsilyloxy, and 1-Oxa-3, 4-diazacyclopentadiene were absent from Methylene Blue after Fenton oxidation.

The GC–MS spectrum showed various peaks indicating the partial mineralization of RB5 after the Fenton process. The retention time of peaks and suggested molecular weight indicated that in the Fenton process, RB5 and Methylene blue were most likely broken down into compounds with lower molecular weight. It also suggested that decolourization was related to the breaking of azo bonds which are associated with chromophores, i.e. conjugated unsaturated bonds (–N=N–) in the molecule (Meric, Kaptan, and Olmez, 2004; Muruganandham and Swaminathan 2004). The products of Fenton oxidation are non-toxic and environmentally friendly. If the products are discharged at this level, it poses no threat to the environment.

Table 2 Methylene Blue before Fenton Reaction by GC-MS Analysis

S/N	Compounds	Retention Index	% Compounds	Mass spectra data
1.	1,2-cyclopentanedione, 3-methyl	1003	15.9	55,69,97,111,**112**
2.	2-Propanol, 1-bromo-	778	5.5	45,60,81,124,**138**
3.	2-cyclopenten-1-one, 2-hydroxy-3,4 dimethyl-	1033	5.8	45,69,97,**126**
4.	Methacrylic acid, ethyl ester	752	10.4	45,69,71,86,**114**
5.	3-Butenoic acid	765	9.0	45,58,69,72,**86**
6.	Propane, 1-methoxy-2,2-dimethyl	609	16.3	45,57,71,87,**102**
7.	1,3-Benzenediol, O-isobutyryl-O'-methoxya	1750	0.9	45,71,92,124,154,**252**
8.	1-Oxa-3,4-diazacyclopentadiene	629	3.3	42,45, 69, **70**
9.	2,4,5,7-Tetramethyl-1,2,3.4-tetrahydropyrimido	1868	3.1	45,55,77,115,185,**228**
10.	Cyclohexene,3-butyl-3-methyl-1-trimethylsilyloxy	1409	2.2	45,61,73,183,207,**240**
11.	2,4,6-Cycloheptatrien-1-one,3,5-bis-trimethylsiyl	1354	27.1	45,59,73,96,207,**250**

Table 3 Reactive Black 5 before Fenton Oxidation by GC-MS Analysis

S/N	Compounds	Retention Index	% Compounds	Mass spectra data
1.	Acetic acid, methoxy	752	0.8	45,63,78, **90**
2.	Acetic acid, anhydride with formic acid	675	0.6	45,60,72,87,**88**
3.	Muramic acid	2221	0.7	45,60,84,114,**251**
4.	Muramic acid	2221	0.6	45,56,72,114,**251**
5.	2-Imidazolidinone, 1,3-dimethyl	1033	1.7	45,56,72,85,**114**
6.	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	972	4.2	55,69,83,**112**
7.	Ethanone, 1-(1-cyclohexen-1-yl)	1027	2.6	45,67,81,109**124**
8.	2-imidazolidione, 1,3-dimethyl	1033	1.3	44,56,72,85,99,**114**
9.	Maltol	1063	1.2	43,71,97,**126**
10.	2-Heptanol, 5-ethyl	1014	0.8	45,69,84, 98,144
11.	4-Pyrimidinecarboxylic acid	1374	0.6	45,59,70,85,113,**172**
12.	Acetic acid	576	0.7	45,60,71,84,**102**
13.	Methacrylic acid, ethyl ester	752	3.1	45,69,86,99, **114**
14.	Isosorbide	1216	1.4	45,69,73,86,103,**146**
15.	Methoxyacetic acid, 6-ethyl-3-octyl ester	1428	1.0	45,57,71,85,127,141,**230**
16.	Ethanol, 2-(2-propenyloxy)	827	0.9	45,58,71,101,**102**
17.	2,2-Dimethyl-3-hydroxypropionaldehyde	865	5.0	56,72,84,**102**
18.	3-Amino-2,6-dimethoxypyridine	1364	0.7	45,,53,66,80,96,139, **154**
19.	1-Propanone, 1-cyclopro,pyl	756	0.7	45,69,95,**98**
20.	Propanoic acid	676	0.8	45,57,**74**
21.	Beta-D-Glucopyranose,1,6-anhydro	1404	1.0	**45,162**
22.	9-Acetyl-S-octahydrophenanthrene	2001	1.2	45,63,77,91,128,213,**228**

23.	Cis-1-(4-Isopropylphenyl)-3-(2-furyl)cyclopropane	1726	1.0	45,57,77,91,128,155,**226**
24.	Isophthalicacid, allyl dodecyl	2723	4.9	55,69,83,111,133,149,**374**
25.	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo(1,2-pyrazine)	1898	2.0	45,70,96,124,194, **250**
26.	Lanosterol	2882	47.1	43,69,81,95,109,**246**
27.	1,4-Bis(trimethylsilyl)benzene	1124	2.4	45,59,73,96,148,**222**
28.	1,4-Bis(trimethylsilyl)benzene	1124	9.7	45,59,73,96,148,**222**

Table 4 Products of Methylene Blue after Fenton Oxidation by GC-MS Analysis

S/N	**Compounds**	**Retention Index**	**% Compounds**	**Mass spectra data**
1.	1,2-cyclopentanedione, 3-methyl	1003	9.6	55,69,97,111,**112**
2.	2-Propanol, 1-bromo-	778	13.8	45,60,81,124,**138**
3.	4-Hexen-3-one, 2,2-dimethyl-	876	16.9	45,69,98,**126**
4.	Isosorbide	1216	11.6	44,69,86,103,**146**
5.	Propane, 1-methoxy-2,2-dimethyl-	609	36.9	57,71,87,**102**
6.	1,3-Benzenediol, O-isobutyryl-O'-methoxya	750	2.6	45,71,92,124, 182,**252**
7.	Vinyl ether	475	8.2	43,69,**70**

Table 5 Products of Reactive Black 5 after Fenton Oxidation by GC-MS Analysis

S/N	**Compounds**	**Retention Index**	**% Compounds**	**Mass spectra data**
1.	1,2-Cyclopentanedione, 3-methyl-	1003	8.0	55,69,83,97,**112**
2.	2-Propanol, 1-bromo-	778	7.0	45,58,81,105,**138**
3.	2-Imidazolidinone, 1,3-dimethyl-	1033	3.1	44,56,72,85,99,**114**
4.	Acetic acid	576	3.2	43,**60,**71,84
5.	Acetic acid	576	3.3	43,**60,**71,84
6.	Methacrylic acid, ethyl ester	752	7.1	69,86,99, **114**
7.	Isosorbide	1216	4.6	44,69,73,86,115,**146**
8.	2,2-Dimethyl-3-hydroxypropionaldehyde	865	18.4	56,72,84, **102**
9.	Propanoic acid	676	2.5	57, **74**
10.	beta.-D-Glucopyranose, 1,6-anhydro-	1404	7.8	60,73, 97,**162**
11.	1,3-Benzenediol, O-isobutyryl-O'-methoxya	1750	3.7	45,71,92,124,154, **252**
12.	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-di-Pyrrolo	1898	6.9	70,96,124,137,166,194, **250**
13.	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydr	1699	2.9	70,86,98,125,195, **210**

IV. CONCLUSION

This study investigated the removal efficiency of color and chemical oxygen demand (COD) from solutions containing Reactive Black 5 and Methylene Blue through the application of the Fenton oxidation process. Key operational parameters, including dye concentration, $FeSO_4$ and H_2O_2 dosages, reaction time, temperature, and pH, were systematically optimized.

The treatment performance was evaluated using UV-visible spectrophotometry and COD analysis. Optimal conditions were established for each parameter to achieve maximum degradation efficiency. Furthermore, GC-MS analysis was conducted to verify the formation of non-toxic degradation products from both dyes.

The findings demonstrate that the Fenton oxidation process is effective not only in achieving complete decolorization but also in promoting partial mineralization of Reactive Black 5 and Methylene Blue into environmentally benign compounds.

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