

WASTEWATER TREATMENT USING ADVANCED OXIDATION PROCESSES

A PROJECT REPORT

Submitted in partial fulfilment for the award of the degree of

Bachelor of Technology (B. Tech)

in

Chemical Engineering

by

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MAY 2017

DECLARATION BY THE CANDIDATE

I here by declare that the project report entitled “**Wastewater Treatment using Advanced Oxidation Processes**” submitted by me to Vellore Institute of Technology University, Vellore in partial fulfillment of the requirement for the award of the degree of **Bachelor of Technology (B.Tech) in Chemical Engineering** is a record of bonafide project work carried out by me under the guidance of **Professor Babu Ponnusami**. I further declare that the work reported in this project has not been submitted and will not be submitted, either in part or in full, for the award of any other degree or diploma in this institute or any other institute or university.

Place : Vellore

Signature of the Candidate

Date: 5th May 2017



School of Civil and Chemical Engineering

(SCALE)

CERTIFICATE

This is to certify that the project report entitled “**Wastewater Treatment using Advanced Oxidation Processes**” submitted by **Tanuj Agarawal (13BCH0056)** to Vellore Institute of Technology University, Vellore, in partial fulfilment of the requirement for the award of the degree of Bachelor of Technology (B. Tech) in Chemical Engineering is a record of bonafide work carried out by him under my guidance. The project fulfils the requirements as per the regulations of this Institute and in my opinion meets the necessary standards for submission. The contents of this report have not been submitted and will not be submitted either in part or in full, for the award of any other degree or diploma and the same is certified.

Professor Babu Ponnusami

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ABSTRACT

Waste water from textile industry is one of the major concern in environment. Although some of the sludge is disposed in an engineered landfill, much of the sludge is openly dumped, which leads to soil, surface water and ground-water contamination. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, high chroma, high COD and BOD concentration as well as much more hard-degradation materials. Effluent from textile mills also contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat.

We used methylene blue to prepare the synthetic waste water. Methylene Blue dye is an aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$ and finds uses in fields of biology and chemistry. It is used in paper and pulp industries, leather industries and can also be used for medicinal purposes. This project focuses on the degradation of methylene blue using Advanced Oxidation processes such as Fenton Process and experiments were carried out to optimise the parameters.

The operating parameters selected for the study are H_2O_2 concentration, Fe^{2+} concentration, initial solution pH, and initial dye concentration. The optimum

operating conditions were obtained by keeping the other parameters as constants. The optimum condition is found to be 100ppm of H_2O_2 , 30ppm of Fe^{2+} , 10ppm of initial dye concentration, and at 6pH. At this condition, 95.9% removal of dye was observed in 60 minutes.

Kinetic studies were carried out in optimum conditions. It was found that the dye degradation by Fenton Process follows two-stage process. Initially it follows 1st order (upto 5 minutes) kinetics and later it follows 2nd order kinetics.

Effect of temperature on degradation studies shows that the degradation follows endothermic reaction.

The conversion rate of Methylene blue was increased and accelerated due to the addition of microwave irradiation and maximum percentage conversion of 96% was reached in 5 minutes. The result shows that microwave assisted Fenton process will be effective for degradation of the dye.

Table of contents

Chapter No.	Title	Page No.
	ABSTRACT	v
	LIST OF TABLES	ix
	LIST OF FIGURES	x
1	Introduction	1
	1.1 Classification of dyes	1
	1.1.1 Reactive dyes	2
	1.1.2 Disperse dyes	2
	1.1.3 Sulphur dyes	2
	1.1.4 Cationic dyes	2
	1.1.5 Acid dyes	3
	1.1.6 Organic dyes	3
	1.1.7 Azoic dyes	3
	1.2 Methylene Blue	3
	1.3 Fenton Process	4
	1.4 Microwave Fenton Process	4
	1.5 Scope of the study	5
	1.6 Objective of the study	5
2	Literature review	6
	2.1 Introduction	6
	2.2 General methods used for treatment of dye effluents	6
	2.2.1 Physical Process	6
	2.2.2 Physio-chemical process	8
	2.2.3 Electrochemical Process	8
	2.2.4 Biological Process	8
	2.2.5 Chemical Process	9
3	Materials and Method	14

	3.1 Materials and chemicals	14
	3.2 Properties and structure of dye	14
	3.2.1 Name and colour	14
	3.3.2 Structure of M.B	14
	3.3.3 General Properties	14
	3.3.4 Preparation of stock solution	15
	3.3 Experimental Procedure	15
	3.3.1 Fenton Process	15
	3.3.2 Microwave Fenton process	16
	3.4 Analytical Technique	16
	3.4.1 Ultraviolet and visible absorption spectroscopy	16
	3.5 Kinetic study	16
4	Results and Discussions	18
	4.1 Construction of calibration curve	18
	4.2 Fenton Process	19
	4.2.1 Effect of Ferrous ions	19
	4.2.2 Effect of pH	20
	4.2.3 Effect of H ₂ O ₂	22
	4.2.4 Effect of dye concentration	23
	4.3 Kinetic studies	25
	4.3.1 At 25 ⁰ C	25
	4.3.2 At 30 ⁰ C	27
	4.3.3 At 40 ⁰ C	29
	4.4 Activation Energy	32
	4.5 Gibbs Free energy	34
	4.6 Microwave Fenton Process	35
5	Conclusion	37
	REFERENCES	38

List of tables

Table No.	Topic	Page No.
Table 4.1.	Calibration curve data	18
Table 4.2.	Effect of Fe^{2+} concentration on dye removal	19
Table 4.3.	Effect of pH variation on dye removal	21
Table 4.4.	Effect of H_2O_2 concentration on dye removal	22
Table 4.5.	Effect of dye concentration on dye removal	23
Table. 4.6.	Values of k and R^2 for first 5 minutes and after 5 minutes	31
Table 4.7(a)	Gibbs free energy before 5 minutes	34
Table 4.7(b)	Gibbs free energy after 5 minutes	34
Table 4.8.	Percentage removal of dye for Microwave- Fenton Process	36

List of figures

Figure No.	Topic	Page No.
Fig 3.1.	Structure of Methylene Blue	14
Fig.3.2.	UV- vis Spectroscope	16
Figure 4.1	Absorbance vs Concentration of Methylene blue	18
Figure 4.2.	Effect of Fe^{2+} concentration on dye removal	20
Figure 4.3.	Effect of pH variation on dye removal	21
Figure 4.4.	Effect of H_2O_2 concentration on dye removal	22
Figure 4.5(a).	Effect of dye concentration on dye removal	24
Figure 4.5(b).	Decolourization of methylene blue after Fenton process	24
Fig. 4.6(a).	1 st order before 5 minutes	25
Fig. 4.6(b).	2 nd order before 5 minutes	26
Fig. 4.6(c).	1 st order after 5 minutes	26
Fig. 4.6(d).	2 nd order after 5 minutes	27
Fig. 4.7(a).	1 st order before 5 minutes	27
Fig. 4.7(b).	2 nd order before 5 minutes	28
Fig. 4.7(c).	1 st order after 5 minutes	28
Fig. 4.7(d).	2 nd order after 5 minutes	29
Fig. 4.8(a).	1 st order before 5 minutes	29
Fig. 4.8(b).	2 nd order before 5 minutes	30
Fig. 4.8(c).	1 st order after 5 minutes	30
Fig. 4.8(d).	2 nd order after 5 minutes	31
Fig. 4.9 (a)	1 st order before 5 minutes	32
Fig. 4.9 (b)	2 nd order after 5 minutes	33
Fig. 4.10 (a)	Decolorization of dye after Microwave-Fenton process	35
Fig. 4.10(b)	Percentage removal of dye for Microwave- Fenton Process	36

CHAPTER 1

INTRODUCTION

Wastewater discharged from industries like textile, leather, paper, and plastics is a serious contamination for environment. The release of these coloured wastewaters into the environment will destroy the ambient ecological equilibrium and threaten the health of human beings. Synthetic or manufactured dyes are visible pollutants which are undesirable and poisonous even at trace levels or at very small amount because of its chemistry and appearance. Many dyes are dissolved in water and made water soluble to meet the colour requirements of most fabrics and with the high rate of increase in urbanization and industrialization the rate of removal of trace amounts of toxic and poisonous pollutants in the ppm and ppb range from the industrial wastewater and contaminated groundwater is increasingly and progressively becoming significant and critical. Numerous technologies such as biodegradation, chemical oxidation, electrochemical oxidation, adsorption, and photocatalytic degradation have been investigated to remove these organic pollutants from aqueous solutions. However, these methods are limited by long processing period, low efficiency, high cost, or secondary pollution. As an advanced oxidation technology, Fenton process is an attractive treatment for organic wastewater because of its effective degradation, low toxicity, and offer a cost-effective source of hydroxyl radicals with easy operation.

1.1 CLASSIFICATION OF DYES

Dyes may be classified according to their chemical structure or by their usage or application. The former approach is adopted by dye chemists who use terms such as azo dyes, anthroquinone dyes and pthalocyanine dyes. The Latter approach is used predominantly by the dye technologist, who speaks reactive dyes for cotton and disperse dyes for polyester and these dyes form a covalent bond with the fibre, usually cotton although they are used to a small extent on wool and nylon. (Sumartono and Andayani, 2011). Various types of dyes used in industries are

- Reactive dyes
- Disperse dye
- Sulphur dyes
- Acid dyes
- Basic (cationic) dyes
- Organic dyes
- Azoic dyes

1.1.1. Reactive dyes

These dyes form a covalent bond with the fibre, usually cotton although they are used to a small extent on wool and nylon. The dye molecule contains specific functional groups which can undergo addition or substitution reactions with the OH, SH and NH₂ groups present in textile fibres. The most important distinguishing feature of reactive dyes is that they form covalent bonds with the substrate which is to be coloured during the application process.

1.1.2. Disperse dyes

These are water- insoluble non-ionic dyes for application to hydrophobic fibres from aqueous dispersion. They are used mostly on to a lesser extent on nylon, cellulose, cellulose acetate and acrylic fibres. Thermal transfer printing and dye diffusion thermal transfer processes for electronic photography represent this dye.

1.1.3. Sulphur dyes

These dyes are applied to cotton from an alkaline reducing bath with soluble sodium sulphide as the reducing agent. This is a relatively small group of dyes. The low cost and good wash fastness properties of the dyeing make this class important from an economic point of view. They are generally macromolecular, coloured compounds which are produced by bridging aromatic amines, phenols and amino phenols with sulphur or sodium polysulfide.

1.1.4. Cationic dyes

These water – soluble cationic dyes are applied to paper, polyacrylonitrile, modified nylons and modified polyesters. Basic dyes yield coloured cations in solution. For this reason they are frequently used as cationic dyes. The principal chemical classes are diazahemicyanine,

triarylmethane, cyanine, hemicyanine, thiazine, oxazin and acridine. These are generally form positively charged dye ions by dissociation, and the positive electric charge is delocalized over the entire molecule.

1.1.5. Acid dyes

These are water – soluble cationic dyes which are applied to nylon, wool, silk and modified acrylics. They are also used to some extent on paper, leather, inkjet printing food and cosmetics. Although they penetrate well into the capillaries of the fibres, no fixed bond is formed and there is virtually no formation of a charge – transfer.

1.1.6. Organic dyes

The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of colours, and they impart better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process.

1.1.7. Azoic dyes

Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dye bath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final colour is controlled by the choice of the diazoic and coupling components.

1.2. METHYLENE BLUE:

We used Methylene blue to prepare our synthetic waste water. Methylene Blue is a heterocyclic chemical compound which is aromatic in nature and its molecular formula is $C_{16}H_{18}N_3S$. Methylene blue is a dye widely utilized for colouring, printing silk and cotton etc. It is likewise useful for medicinal purposes because of its antiseptic properties. It is also used in treatment of leather, and in paper and pulp industries. The dye was prepared by treating 4-aminodimethylaniline with hydrogen sulphide, dissolved in hydrochloric acid, after which

oxidation with ferric chloride was done. Methylene blue concentration was measured at 664nm. The absorption rate depends on factors like protonation and adsorption.

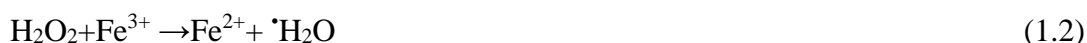
1.3. FENTON PROCESS:

Fenton's Reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$): Fenton's reagents are Hydrogen Peroxide (H_2O_2) and Ferrous Ions (Fe^{2+}). The reaction of these two reagents produces highly reactive hydroxyl radicals ($\cdot\text{OH}$). The hydroxyl radical is a strong oxidant which can oxidize various organic compounds. Fenton's Reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (Shaobin wing, 2008).

Chemistry of Fenton Process: Fenton process is based on electron transfer between hydrogen peroxide (H_2O_2) and a homogeneous metal catalyst (Fe^{2+}). In Fenton process, hydrogen peroxide is catalysed by ferrous ions to produce hydroxyl radicals.



This reaction is propagated by ferrous ion regeneration, which is mainly due to the reduction of the produced ferric species with hydrogen peroxide.



The Fenton process is very effective for hydroxyl radical's generation but it involves consumption of one molecule of Fe^{2+} for each $\cdot\text{OH}$ radical produced, which demands high concentration of Fe^{2+} concentration.

1.4. MICROWAVE FENTON PROCESS:

Microwave has been widely used to enhance and accelerate the heating process and catalytic degradation activity due to its special heating mechanism. The advantages of microwave heating techniques are rapid and selective heating, ease of control, and enhanced chemical reactivity (Shu-Ting Liua et al, 2013).

1.5. SCOPE OF THE STUDY

- Reactive dyes are most widely used in textile industries and it is taken for the study
- Fenton process is one of the effective method compared to the other conventional methods like biodegradation, adsorption, photocatalytic degradation etc for the removal of organic waste from water with high efficiency, low cost and high degradation.
- Further we did Microwave assisted Fenton process to improve the efficiency of the degradation to up to 97% to produce clean water that can be further reused and recycled in industries.

1.6. OBJECTIVE OF THE STUDY

- To study the dye degradation by Fenton process and optimize the operating parameters
- To find the activation energy required for degradation of dye
- To check the effectiveness of Microwave assisted Fenton process

CHAPTER 2

LITERATURE REVIEW

2.1. INTRODUCTION

Treatment of industrial wastewater is one of the major concerns. Dyes are one of the main pollutants in industrial wastewater. The common processes of degradation and discoloration on modern dyes are ineffective because of high degree of aromatic groups in dye molecules.

Among various ways for heating dye solution, Advanced Oxidation Process (AOP's) is considered to be the simple and cheap method. In order to increase the effectiveness of this process, it is accompanied in the presence of ultra violet rays and effective adsorbent is analysed.

2.2 GENERAL METHODS USED FOR TREATMENT OF DYE EFFLUENTS

The following methods are used to treat dye effluents.

- Physical process
- Physio-chemical process
- Electrochemical process
- Biological process
- Chemical process

2.2.1 Physical Process

Activated carbon is widely used for method of dye decolourization by adsorption, and is very effective for adsorbing cationic, mordant and acid dyes. Numerous other adsorbents, such as pea, woodchips, fly ash and brown coal have been used as dye adsorbents. Nanofiltration removed up to 99% of a variety of reactive dyes in laboratory studies and has been successfully applied in a pilot-scale study employed a microfiltration unit followed by a nano filtration unit or a reverse osmosis membrane processes for large flow rates is prohibitively costly.

Saeed B.Bukallah et al, 2006, studied about removal of Methylene Blue (MB) dye from aqueous solution onto sand surface was carried out at room temperature. The conditions of

maximum adsorption of the dye were optimized. It was seen that under optimized conditions, up to 92% dye can be removed from solution onto the sand surface. The adsorption data were fitted to Freundlich isotherm which showed that adsorption was monolayer in nature. Furthermore, the Dubinin - Radushkevich equation revealed that the adsorption process was physical in nature. The adsorption of the dye decreased in the presence of thiosulphate, potassium, nickel and zinc ions.

Rauf M.A, 2009, studied that synthetic dyes are a major part of our life as they are found in the various products ranging from clothes to leather accessories to furniture. An unfortunate side effect of their widespread use is the fact that up to 12% of these dyes are wasted during the dyeing process, and that approximately 20% of this wastage enters the environment (mostly in water supply). He stated that that TiO_2 can be used as an effective catalyst for the degradation/decolouration of various dyes in solution. The findings also indicate that degradation rate can be influenced by operational parameters such as the amount of a photo catalyst, pH and concentration of organic dyestuff besides the presence of electron acceptors and other additives. The TiO_2 sample when loaded with metal ions enhances its photocatalytic activity. Cationic dye undergoes faster degradation than the anionic dyes.

Senthil Kumar et al, 2010, showed that Cashew Nut Shell (CNS) can be employed as a low cost alternative compared to other commercial adsorbents in the removal of dyes from wastewater. The experimental data were analysed by Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, Toth, Temkin and Dubinin–Radushkevich adsorption isotherms. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. Pseudo-first-order, pseudo second- order and intra-particle diffusion models were used to fit the experimental data. The effect of pH of aqueous solution decreases the removal efficiency with the increase in pH due to the ionic effect. The % CR (Congo red dye) removal increases from 56.33 to 99.34% for an increase in adsorbent dose from 5 to 30 g/L because of the concentration gradient between CR concentration in the solution and the CR concentration in the surface of the CNS. The temperature has adverse effect on the percentage of dye removal due to the decreased surface activity suggesting that adsorption between CR and CNS was an exothermic process. The thermodynamic analysis indicates that the system is spontaneous and exothermic. The CNS appeared to be suitable for the removal of CR from aqueous solutions.

2.2.2 Physio-chemical process

José Blanco and Meritxell, 2012, studied how coagulation and flocculation are used to remove the insoluble and colloidal heavy metal precipitates formed during the precipitation step. Colloidal heavy metal precipitates are tiny particles that possess electrical properties, which create repelling forces and prevent agglomeration and settling. Coagulation is the process of making the particle less stable by neutralizing its charge, thus encouraging initial aggregation of colloidal and finely divided suspended matter. Particles no longer repel each other and can be brought together.

When suspended in water, the charge on organic and inorganic colloids is typically negative. Because of electrostatic forces, the negative colloid charge attracts positive ions

2.2.3. Electrochemical process

Gomathi and Eraiah Rajashekhar, 2012, studied how direct current is applied between two electrodes, viz, anode and cathode, to generate redox agents, which react with organic compounds in the effluents. The electro oxidation method requires use of stable anodes. Some of the significant advantages of this method are that there is little or no consumption of chemicals, sludge built up is low and intermediates are generally not hazardous. It shows efficient and economical removal of dyes and a high efficiency for degradation of recalcitrant pollutants. The cost of electricity used in this method is comparable to the price of chemicals employed in other methods

2.2.4. Biological process

The application of microorganisms for the biodegradation of dyes is an attractive and simple method of operation and offers considerable advantages. The process is relatively expensive, the operational costs are low and the end products of complete mineralization are not toxic.

Although many microorganisms are capable of cleaving chromophores and auxochromes of some dyes, few can mineralize dyes to CO₂ and H₂O, apparently, which is due to the complex structure of dyes. Most decolourization occurs anaerobically, though there are few bacterial species that can decolorize dye waste aerobically.

2.2.5. Chemical process

Babuponnusami A and Muthukumar K, 2014, have discussed about advanced oxidation processes which are found to be an environmental friendly process for the degradation of refractory compounds. Different AOP's have been reported to select the most appropriate technique for the specific treatment.

Mohammadine et al, 2013, have studied about degradation of Reactive yellow by Fenton reagent. They have remarked that Optimal operation parameters for the Fe^{2+} and H_2O_2 concentration, reaction time, pH and temperature were 25mg/l, 250mg/l, 20minutes, pH3 and 293K respectively for 85% decolourization of Reactive yellow 84(dye).

Sanjay R.Thakare, 2004, in his journal 'Catalytic degradation of methylene blue by Fenton like System' proposed the degradation of dye starts with Fe(III) rather than Fe(II) is more promising. The pH plays an important role during the degradation reaction. The present study reflects that Fenton's reaction is more efficient in the presence of small amount of salicylic acid is added which is one of the priority pollutant.

Hesham and Saied, 2010, showed that increase in extent of decolourisation of the dye was observed when the reaction temperature was raised. The results indicate that the optimum pH for the decolourization of all dyes examined is in the range between 3 and 4. The rate of decolourization showed a remarkable dependence on the initial Fe^{3+} concentration. Using dilute dye solutions in the range of $(0.30\text{--}1.50 \times 10^{-5} \text{ mol dm}^{-3})$ the rate increased as the Fe^{3+} concentration was increased from 1.5×10^{-4} to $6.0 \times 10^{-4} \text{ mole dm}^{-3}$, and becomes practically constant when it exceeds $6.0 \times 10^{-4} \text{ mole dm}^{-3}$. Below $1.5 \times 10^{-4} \text{ mole dm}^{-3}$ of Fe^{3+} , the decolourization reaction is too sluggish to account for any practical significance. But the decolourization rate of all examined dyes decreased at high Fe^{3+} concentrations ($\geq 1.0 \times 10^{-3} \text{ mole dm}^{-3}$). There is an optimum H_2O_2 concentration in the range of 0.01–0.04 mole dm^{-3} that is effective for decolourization of the dyes. The results will be useful for designing the treatment systems of various dye-containing wastewaters. It was also found that the decolourisation of the dyes undergoes a fast reaction than the mineralization.

Arturo A.Burbano et al, 2004, concluded an effective in situ treatment of methyl tert-butyl (MTBE) contaminated groundwater. Initial MTBE concentrations $[MTBE]_0$ of 1.0 and 2.0 mg/L were treated with Fenton reagent (FR) using a $[FR]_0:[MTBE]_0$ molar ratio of 10:1. FR was used in equimolar mixture of Fe^{2+} and H_2O_2 i.e 1:1. This analysis considers the hydroxyl radicals ($OH\cdot$) produced by FR as the main species responsible for degradation process. MTBE transformation followed pseudo-first order kinetics, while the subsequent phase exhibited a sharp drop in degradation rate and had most negligible contribution to overall degradation. Experiments performed at acidic pH exhibited the best degradation results while at neutral pH the degradation rates dropped significantly.

Merzouk et al, 2008, showed that colour induced by a red dye was effectively removed (with a removal yield higher than 85%) for wastewater with a COD of 2500mg/L and a dye concentration lower than 200mg/L when pH ranged from 6-9, residence time was 14min, current density was 31.28mA/cm² and water conductivity was 2.4 mS/am for an inter-electrode distance of 1cm, gave access to a dye removal efficiency between 85 and 95%. Under these conditions, COD abatement was also higher than 80%.

Muhammad A.Rauf et al, 2010, remarked that the adsorption intensity of the dye solution monitored at 668nm decreased with time upon irradiation in the presence of the catalyst Cr–Ti catalyst with 10% Cr^{3+} content (Ti–10Cr) was prepared by sol–gel method and used to degrade Methylene Blue (MB) dye in the presence of UV light. The photo-degradation of the dye molecules in the presence of this catalyst followed the second-order-kinetics with a degradation efficiency of 70% at pH7. The degraded products were analysed by using the LC–UV/vis–MS technique and it was found that the dye initially undergoes demethylation resulting in the formation of some intermediate products

Salman Ashraf.S et al, 2006, studied about degradation of Methyl red using the ferrous-hydrogen peroxide system. The oxidation and subsequent degradation of the dye was found to be dependent on both the amount of Fe^{2+} ions as well as hydrogen peroxide. This approach was found to degrade MR rapidly and efficiently. The discoloration of the dye solution was monitored spectrophotometrically and was found to fit to first-order equation. It is suggested that the photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution. Our study also examined the effect of various ions that are

generally found in textile waste stream, on the decolourization of MR. Interestingly, we found that NaIO_3 adversely affected the discoloration of MR by Fenton reagent, whereas $\text{Ca}_3(\text{PO}_4)_2$ significantly increased the discoloration rate of the dye. Thus some ions and salts that may be present in textile waste streams have the potential to significantly affect the dye degradation rates.

Shaobin Wang, 2008, worked on decolourisation of wastewater using Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) reactions was investigated and compared to that of a typical azo dye, C.I. Acid Black 1, under neutral conditions. The degradation of the dye in the initial stages of the Fenton oxidation was faster than in the Fenton-like oxidation, although the extent of dye degradation in the two processes was very similar after 100 min. The kinetics of Fenton oxidation is complex and can be described by a combined pseudo-first-order kinetic model while the Fenton-like reaction follows comparatively simpler, pseudo-first-order kinetics.. The reaction orders in terms of Fe and H_2O_2 concentrations for both Fenton and Fenton-like oxidations were similar at values of 3 and 0.75, respectively. For the two oxidation systems, dye degradation depends on initial Fe and H_2O_2 concentrations and pH, but temperature has little influence on overall dye degradation in the range 15-45°C.

Gowtham and Pauline, 2015, focused on the suitability of photo-Fenton process for the degradation of methylene blue dye in terms of COD removal and it is optimized for experimental parameters such as pH, H_2O_2 concentration, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration and contact time. The photo-Fenton process is effective under pH 3. The maximum efficiency of COD removal for 50 mg/L of methylene blue is attained at optimum concentration of 10mg/L of H_2O_2 , 50mg/L of Fe^{2+} and contact time of 30 minutes. Fenton process-based advanced oxidation processes are an emerging prospect in the field of dye removal.

Muruganandham et al, 2014, have discussed in their paper about various advanced oxidation processes applied for the degradation of contaminants in wastewater under different experimental conditions. Combined advanced oxidation processes substantially enhanced the degradation rate by generating more reactive radicals under suitable conditions. It has already been established that AOPs are very efficient compared to conventional treatment methods for degradation and mineralization of recalcitrant pollutants present in water and wastewater.

AOPs generate a powerful oxidizing agent, hydroxyl radical, which can react with most of the pollutants present in wastewater.

Babuponnusami and Muthukumar, 2012, showed better performance with simultaneous utilization of UV irradiation and electrolysis with Fenton's reagent. Degradation efficiency was observed in the order: photo-electro-Fenton > sono-electro-Fenton > electro-Fenton > Fenton. Even though complete degradation of phenol was observed with photo-electro-Fenton and sono-electro-Fenton processes, photo-electro-Fenton process showed complete removal of phenol and 64.19% of mineralization within 30 min, whereas in the case of sono-electro-Fenton process, no phenol was detected after 40 min and the mineralization observed at optimum conditions was 67.93%. Fenton and electro-Fenton processes required more time for phenol degradation and mineralization. The optimum electrode distance of 5 cm, Fe^{2+} dosage of 4 mg/L, H_2O_2 concentration of 500 mg/L, initial pH of 3 and current density of 12 mA/cm² were found to give higher phenol degradation and COD removal. The rate constant values at optimum operating conditions were found to be 0.0067, 0.0286, 0.0683 and 0.0934 min⁻¹ for Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes respectively.

Marco Panizza et al, 2006, investigated the direct and indirect electrochemical oxidation of a synthetic solution containing methylene blue. In particular, in the indirect electrolysis, the oxidation of methylene blue only occurred in the presence of chloride ions that acted as redox mediators and the reaction was affected by the chloride concentration and applied current density, while in the direct electrolysis the oxidation took place by reaction with electro generated hydroxyl radicals and was favoured by high flow rates, meaning that the oxidation was a diffusion-controlled process. The comparison of the results showed that faster mineralisation and decolourisation of the solution was achieved by the indirect electrolysis, due to the high bleaching properties of active chlorine.

Sheng and Choc, 1997, have concluded that the experimental results show that there exists an optimal pH at 3 and an optimal temperature at 30°C for the Fenton treatment process. When operated at these optimal pH and temperature conditions, the Fenton treatment process is capable of reducing the COD concentration of the wastewater to the discharge standard. Chemical coagulation using polyaluminum chloride and polymer was found to complement the Fenton treatment process in reducing the floc settling time, enhancing colour removal and

reducing Fe ion concentration. In terms of overall COD removal efficiency, the two step Fenton treatment process intended for chemical coagulation followed by chemical oxidation was found to be marginally better than the single step approach but due to its more complicated operation, use of the two-step treatment process is not warranted. The reaction rate coefficient was strongly dependent on temperature and H_2O_2 and FeSO_4 concentrations.

Kavitha and Palanivelu, 2003, discussed about phenol degradation by different Fenton related processes. They found that increased degradation and mineralisation efficiency were observed in photo-Fenton processes as compared to conventional Fenton process. Solar and UV-Fenton offers 96% mineralisation of phenol within 25 and 15 min respectively whereas only 41% mineralisation occurred by Fenton process. In Fenton process, carboxylic acids like acetic acid and oxalic acid were formed as end products during the degradation of phenol while in photo-Fenton processes, both these ions were identified during the early stages of phenol degradation and were oxidized almost completely at 120min of the reaction time. In photo-Fenton processes (solar and UV light) complete degradation were observed with 0.4 mM of Fe^{2+} catalyst as compared to 0.8 mM of Fe^{2+} in conventional Fenton process. Even though, UV-Fenton offers a slightly better efficiency than solar-Fenton with respect to mineralisation rates, the intrinsic low-cost associated with solar energy turned out to be efficient in treating phenol as compared to UV light. The use of solar energy in Fenton system offers a promising technology for treating phenols in wastewater for tropical countries like India, where solar energy is abundant.

Shu-Ting Liu et al, 2013, studied about the conversion rate of Methylene blue (MB) was increased and accelerated due to the assistance of microwave irradiation, with value of 95.0% after heated for only 1 min even higher than that of treated by traditional Fenton process for 60min. The MB conversion increases with initial concentrations of H_2O_2 and Fe^{2+} because of the increased generation of hydroxyl radicals. Due to the fast and selective heating of water and H_2O_2 molecules, microwave irradiation will significantly accelerate and enhance the MB conversion by Fenton process. With advantages of highly effective and fast processing, the microwave enhanced Fenton process could be a potential technology to remove organic contaminants from wastewater.

CHAPTER 3

MATERIALS AND METHODS

3.1. MATERIALS AND CHEMICALS:

Methylene Blue dye was selected for this study and it is commercially available in the market. Analytical grades of hydrogen peroxide (H_2O_2 35% w/v), ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (NaOH), sulphuric acid were purchased from Merck and used in the study.

3.2. PROPERTIES AND STRUTURE OF THE DYE

3.2.1. Name and colour

Methylene Blue is visible in blue colour and has maximum absorption value of (668nm).

3.3.2. Structure of MB

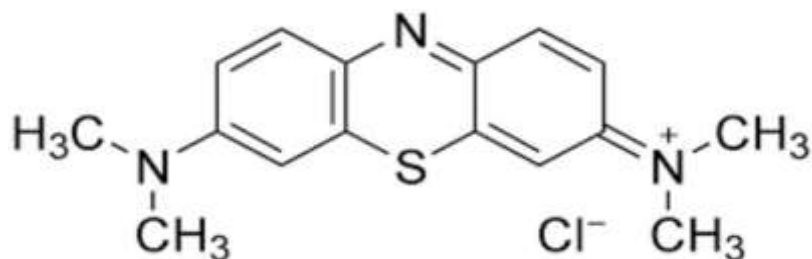


Fig 3.1. Structure of Methylene Blue

3.3.3. General properties:

1. Used in industries like biology and chemistry also can be used in paper and pulp industries, leather industries and can also be used for medicinal purposes.
2. Methylene blue is widely used as a redox indicator. Solutions of this substance are blue when in an oxidizing environment, but will turn colourless if exposed to a reducing agent.

3.3.4. Preparation of stock solution:

100 ppm of dye stock solution were prepared by weighing 0.01g methylene blue and dissolving it in distilled water. From the stock solution required amount of dye solution was prepared.

3.3. EXPERIMENTAL PROCEDURE:

3.3.1. Fenton Process:

The experiments were carried out in a 1L batch type reactor. The contents were stirred well with magnetic stirrer. The effect of pH (3-9), Fe^{2+} concentration (10-40ppm), H_2O_2 concentration (50-100ppm) and initial dye concentration (10-50ppm) were studied. The dye degradation was carried out at room temperature. All the experiments were carried out for the duration of 60mins. Aliquots samples were taken at every 10mins intervals to find the percentage degradation using UV-spectrophotometer. The pH of the solution was adjusted using H_2SO_4 and NaOH solution.

3.3.2. Microwave Fenton process:

To improve percentage degradation, microwave combined with Fenton process was selected. The experiments were carried out with previously optimised parameters (10ppm Dye, 30ppm Fe^{2+} , 100ppm H_2O_2 and 6pH). The readings were taken every 10 minutes for an hour. The absorbance values were noted down. From the calibration graph, the concentration values were found out.

The percentage removal of dye from the solution was found out from the following eqns.

$$\% \text{ Removal} = (C_o - C_f) * 100 / C_o, \text{ where}$$

C_o - initial concentration

C_f - final concentration.

3.4. ANALYTICAL TECHNIQUE:

3.4.1. Ultraviolet and Visible Absorption Spectroscopy

Fig 3.2 shows the UV-vis spectroscope. UV absorption spectroscopy measures the reduction of a beam of light after passing or reflecting from a sample. It is mostly used for organic or inorganic complexes or molecules in solution. It has limited use for sample recognition but its very useful in quantitative measurements. UV spectroscopy range covers 400-900nm. It is helpful in characterizing the absorption, transmission and reflectivity of the organic pollutants and analytes in wastewater.



Fig.3.2. UV-vis Spectroscope

3.5. KINETIC STUDY:

We performed kinetic study for Fenton's process to check the order of the reaction, and hence find the activation energy of the reaction using the k values.

The Fenton oxidation of the dye can be represented by the following nth-order reaction kinetics,

$$dC/dt = -kC^n \quad (3.1)$$

For a first order reaction, the equation is:

$$\ln([A]_t/[A]_o) = -kt \quad (3.2)$$

For a second order reaction, the equation is:

$$1/[A] = 1/[A]_0 + kt \quad (3.3)$$

Kinetic study was performed at three temperatures at optimum reaction conditions. From the values of rate constant, k , we got the activation energy values at three temperatures by plotting graphs between $\ln(k)$ vs $1/T$.

Arrhenius' equation gives the dependence of the rate constant, k of a chemical reaction on the absolute temperature, a pre-exponential factor and other constants of the reaction.

$$k = Ae^{-E_a/(RT)} \quad (3.4)$$

Taking the natural logarithm of Arrhenius' equation yields

$$\ln(k) = -E_a/R (1/T) + \ln(A) \quad (3.5)$$

Then, we plotted a graph of $\ln(k)$ vs $1/T$ to get the value of activation energy for 1st order kinetics (before 5 minutes) and 2nd order kinetics (after 5 minutes).

The following reaction relates the free energy of a reaction to the equilibrium constant of a reaction:

$$\Delta G^\circ = -RT \ln K \quad (3.6)$$

The magnitude of ΔG° tells how far the reaction is from equilibrium. In reactions in which enthalpy is favourable and entropy is unfavourable, the reaction becomes less spontaneous (ΔG° increases) until eventually the reaction is not spontaneous (ΔG° when > 0).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CONSTRUCTION OF CALIBRATION CURVE

A calibration curve of absorbance versus concentration of MB was obtained using UV-spectrometer at the wavelength of maximum absorbance (668nm) and the values are shown in table 4.1 and corresponding graph is shown in figure 4.1.

Table 4.1. Calibration curve data

Concentration(C)	Absorbance(A)
1	0.187
3	0.536
5	0.909
8	1.364
10	1.632
12	1.87
15	2.1

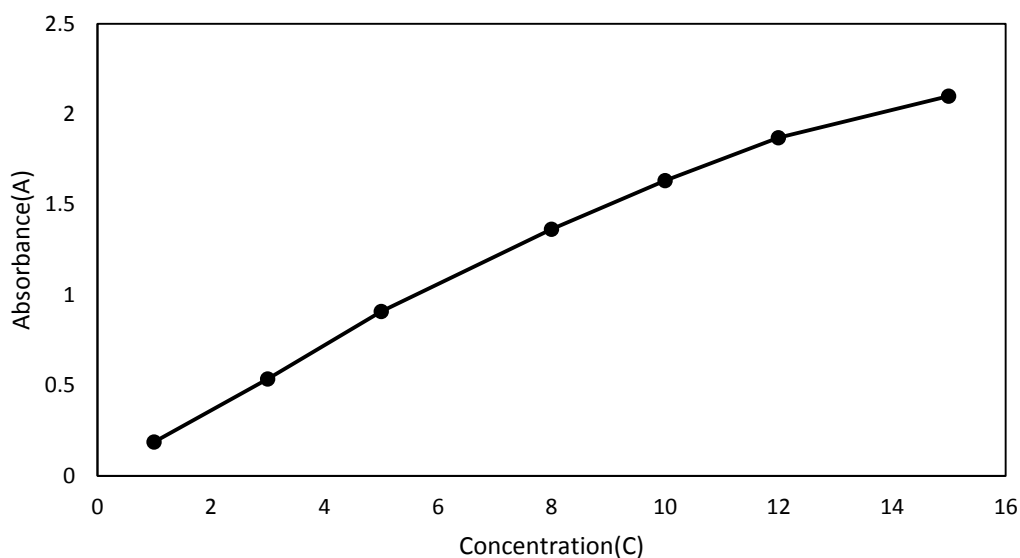


Figure 4.1 Absorbance vs Concentration of MB

4.2. FENTON PROCESS:

In Fenton process Hydrogen peroxide (H_2O_2) reacting with Fe^{2+} ions to create active hydroxyl radical species that oxidize inorganic or organic compounds. In recent past, Fenton reaction was effectively utilised in the treatment of wastewater process for the removal of harmful organics from wastewater. The various factors which are affecting the percentage dye degradation are observed in the following sections.

4.2.1. Effect of Ferrous ions (Fe^{2+})

In Fenton process, hydroxyl radicals production are depends on Fe^{2+} concentration and also it effects the %degradation. Hence effect of Fe^{2+} concentration on percentage degradation was carried out by maintaining other parameters constant. Fe^{2+} concentration was varied from 10ppm to 40ppm and H_2O_2 concentration, pH and initial dye concentration are 10ppm, 100ppm, 3pH respectively. The experimental results are shown in Table 4.2. And figure 4.2.

Table 4.2. Effect of Fe^{2+} concentration on dye removal

time	%dye removal			
min	10ppm	20ppm	30ppm	40ppm
0	0	0	0	0
10	25	72	79	65.8
20	26	73.2	79.8	66.1
30	27	75	80	66.3
40	27.3	76	80.3	67
50	28	76.2	81	67.8
60	28.2	77.9	81.5	68.5

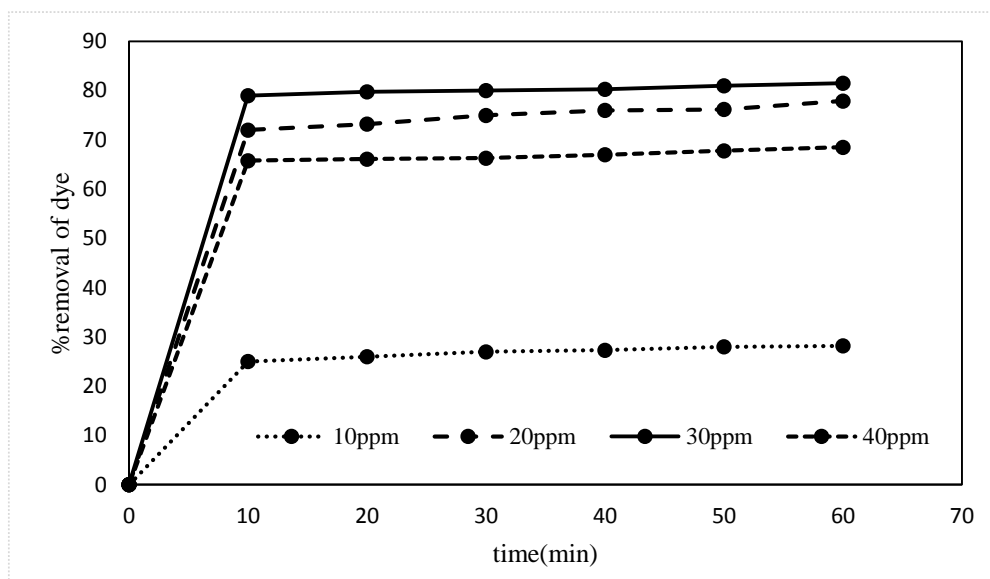


Figure 4.2. Effect of Fe^{2+} concentration on dye removal (dye concentration: 10ppm, pH: 3, H_2O_2 concentration: 100ppm)

From the results it was observed that, the extent of degradation of the dye increased with increasing Fe^{2+} ion concentration. As the Fe^{2+} concentration increased from 10ppm to 30ppm the %degradation was increased from 28.2% to 81.5%. Further increase in Fe^{2+} concentration will decrease the percentage degradation due to self-scavenging effect of Fe^{2+} as shown in Eq 4.1



Hence Fe^{2+} concentration of 30ppm was considered as optimum and used for other experiments.

4.2.2. Effect of pH:

The optimum Fe^{2+} concentration was found to be 30ppm. The pH was varied from 3 to 9. Dye and H_2O_2 concentration was kept at 10ppm and 100ppm respectively. The solution was subjected to continuous stirring using magnetic stirrer. The samples were taken every 10 minutes for an hour. The absorbance values were noted down. From the calibration graph, the

concentration values were found out. The percentage removal of dye from the solution was found out and shown in table 4.3. and figure 4.3.

Table 4.3. Effect of pH variation on dye removal

time	%removal of dye					
min	4pH	5pH	6pH	7pH	8pH	9pH
0	0	0	0	0	0	0
10	79	76.9	92.5	16	87.98	23
20	79.2	76.92	93.2	21	90	37
30	79.5	76.98	94	27	91	39.5
40	80.6	77.9	94.4	29	91.44	39.66
50	81.2	79.5	94.6	37	91.79	45.98
60	82.5	79.71	94.9	47	92.02	51.6

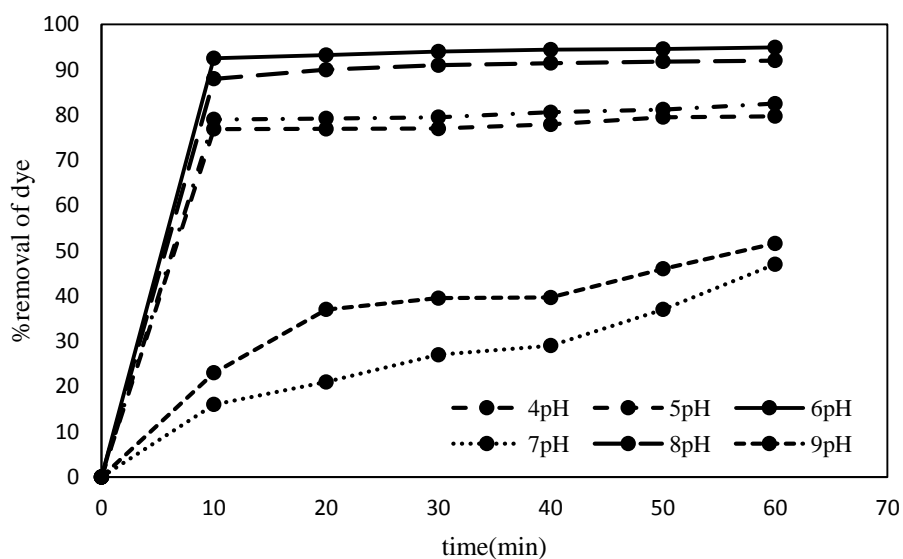


Figure 4.3. Effect of pH variation on dye removal (dye concentration: 10ppm, Fe^{2+} concentration: 30ppm, H_2O_2 concentration: 100ppm)

From the results it was observed that the extent of dye degradation was higher at pH 6. Hence solution of pH of 6 was considered as optimum and was used for other experiments.

4.2.3 Effect of H₂O₂:

The optimum Fe²⁺ concentration was found to be 30ppm. The optimum pH was found to be 6. Then we changed the concentration of H₂O₂ (50, 60, 70, 80, 90, 100 ppm). Dye concentration was kept at 10ppm. The readings were taken every 10 minutes and the corresponding absorbance values were noted down. From the calibration graph, the concentration values were found out. The percentage removal of dye from the solution was found out as shown in the table 4.4. and figure 4.4.

Table 4.4. Effect of H₂O₂ concentration on dye removal

time	% removal of dye					
min	50ppm	60ppm	70ppm	80ppm	90ppm	100ppm
0	0	0	0	0	0	0
10	62.6	57.8	59	42.8	55.8	90.05
20	63.3	58.4	62.6	43.4	56.1	91.15
30	64.2	59	63.7	43.6	56.5	92
40	66.7	60.5	66.6	43.8	56.9	92.5
50	71	63	70.2	44.6	63.4	93.2
60	74.6	64.2	74	48.2	68	94

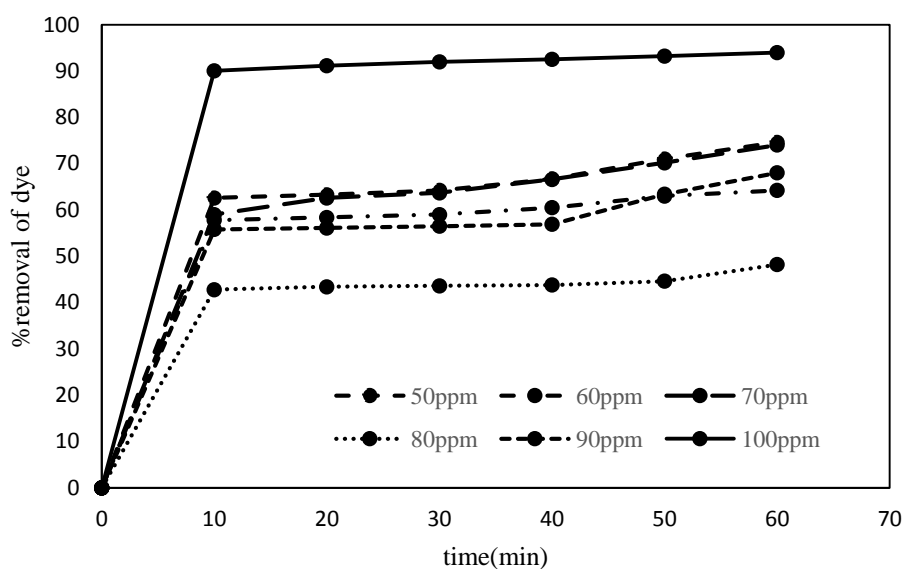


Figure 4.4. Effect of H₂O₂ concentration on dye removal (dye concentration: 10ppm, pH: 6, Fe²⁺ concentration: 30ppm)

Hence, the H_2O_2 concentration of 100ppm was effective in degradation of 94% of dye at 25°C . As you can see higher the concentration of H_2O_2 higher the percentage removal which proves that higher the concentration of H_2O_2 higher the release of hydroxyl ions and hence higher the percentage removal. Therefore, H_2O_2 in high concentration act as a scavenger of highly potent $\text{HO}\cdot$ radical to produce per hydroxyl radical $\text{HO}_2\cdot$.

4.2.4. Effect of dye concentration:

The optimum Fe^{2+} concentration was found to be 30ppm. The optimum pH was found to be 6. The optimum H_2O_2 was found to be 100ppm. The dye concentration was changed from 10ppm to 50ppm. The readings were taken every 10 minutes for an hour. The absorbance values were noted down. From the calibration graph, the concentration values were found out. The percentage removal of dye from the solution was found out as shown in table 4.5. and corresponding graph in figure 4.5(a).

Table 4.5. Effect of dye concentration on dye removal

time	% removal of dye				
min	10ppm	20ppm	30ppm	40ppm	50ppm
0	0	0	0	0	0
5	93.58	91	93.5	94.49	62.6
10	94.8	91.2	93.59	94.57	63.3
20	95.18	92.015	94.35	94.58	64.2
30	95.32	93.95	94.45	94.58	66.7
40	95.56	94.05	94.55	95.238	71
50	95.76	94.25	95.25	95.3046	74.6
60	95.9	94.45	95.5	95.34	75.4

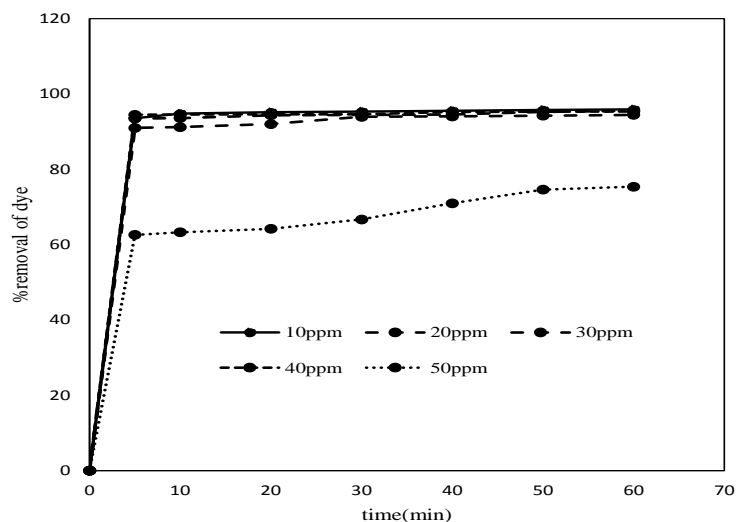


Figure 4.5(a). Effect of dye concentration on dye removal (Fe^{2+} concentration: 30ppm, pH: 6, H_2O_2 concentration: 100ppm)

From the results it was observed that as the concentration increases, %removal of dye decreases which is due to unavailability of oxidising agents at higher concentration of dye. Fig 4.5(b) shows the actual colour changes after the experiments.



Figure 4.5(b). Decolourization of methylene blue after Fenton process

Fig. 4.5(b).shows the colour change of Methylene blue after Fenton process performed for 1 hour.

4.3. KINETIC STUDIES

Kinetic studies were conducted at 25°C, 30°C, and 40°C and keeping other parameters at optimum values (10ppm Dye, 30ppm Fe²⁺, 100ppm H₂O₂, and 6pH).

4.3.1. At 25° C

Experiments were carried out at optimum conditions by maintaining the temperature at 25° C. The experimental were plotted and formed that the dye degradation follows two step process. In first 5 minutes, the degradation rate was very higher but after 5 minutes, the rate of dye degradation was slower. Hence kinetic analysis was carried out in two stages, ie before 5 minutes and after 5 minutes. The results are shown in Fig 4.6.(a),(b),(c),(d). The R² values and rate constant values are tabulated in table 4.6.

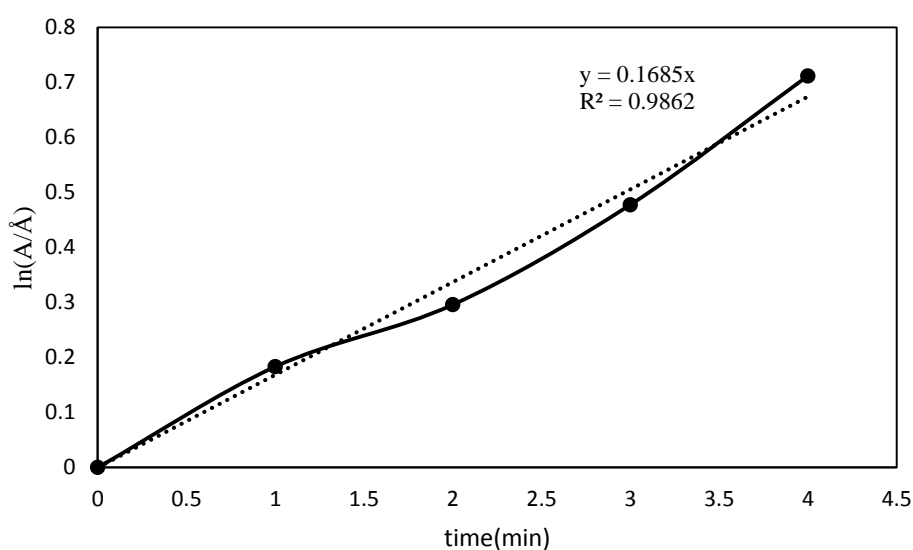


Fig. 4.6(a). 1storder before 5 minutes

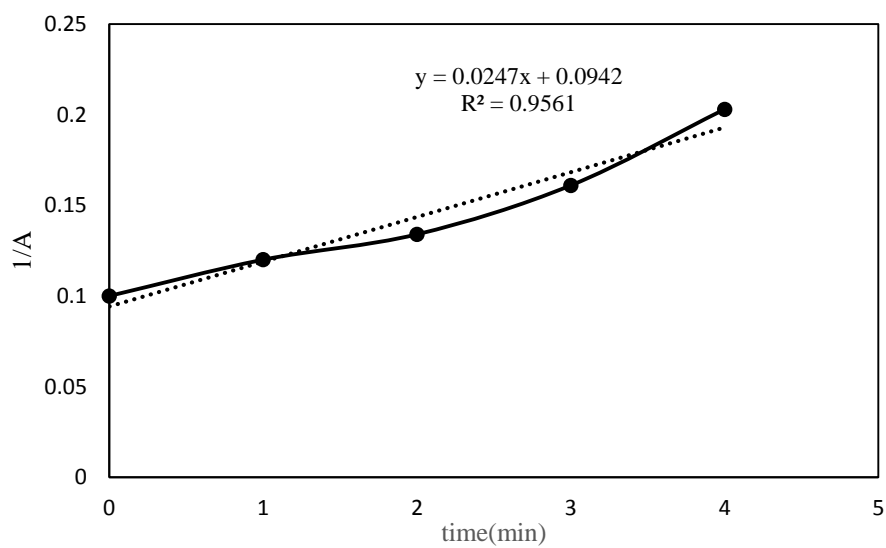


Fig. 4.6(b). 2nd order before 5 minutes

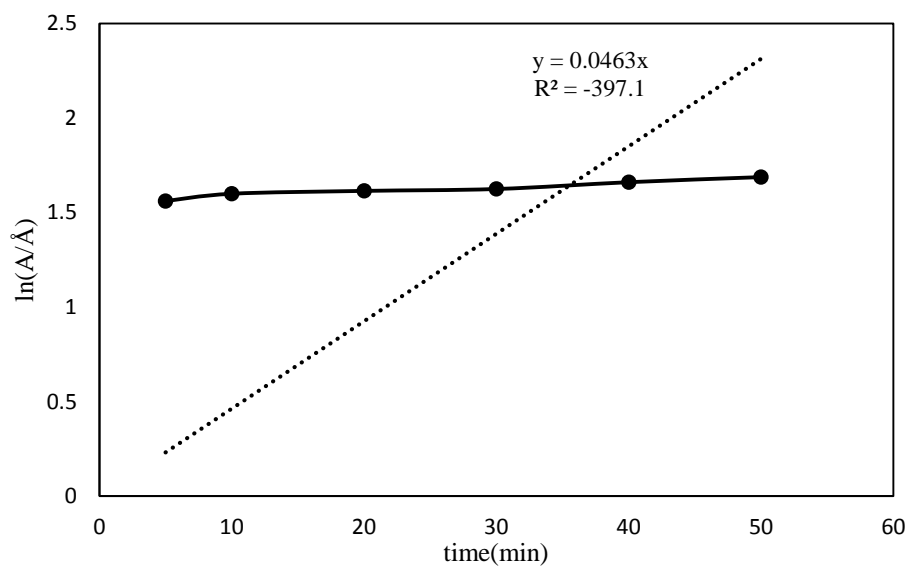


Fig. 4.6(c). 1st order after 5 minutes

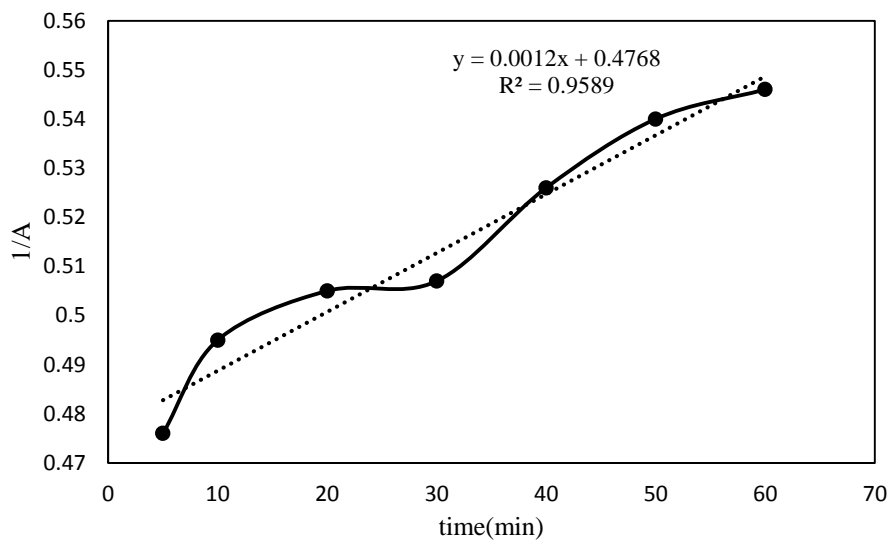


Fig. 4.6(d). 2nd order after 5 minutes

4.3.2. At 30^o C

Experiments were carried out at optimum conditions by maintaining the temperature at 30^o C. The experimental were plotted and formed that the dye degradation follows two step process. In first 5 minutes, the degradation rate was very higher but after 5 minutes, the rate of dye degradation was slower. Hence kinetic analysis was carried out in two stages, ie before 5 minutes and after 5 minutes. The results are shown in Fig 4.7.(a),(b),(c),(d). The R² values and rate constant values are tabulated in table 4.6.

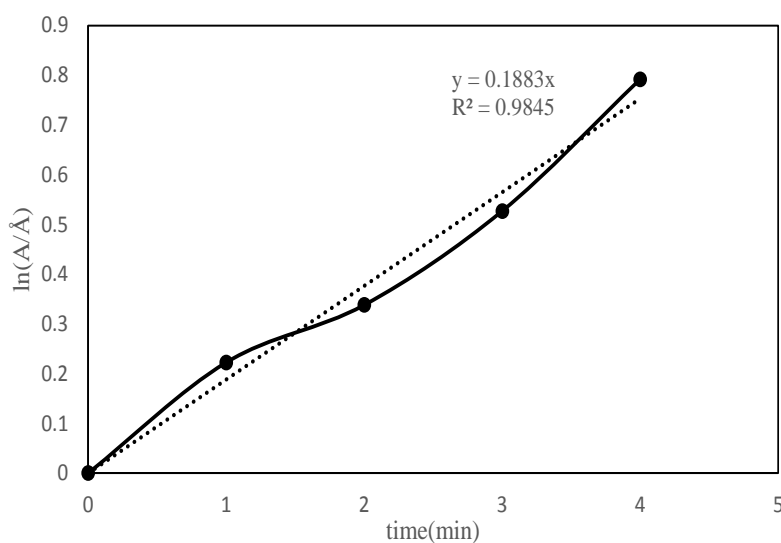


Fig. 4.7(a). 1st order before 5 minutes

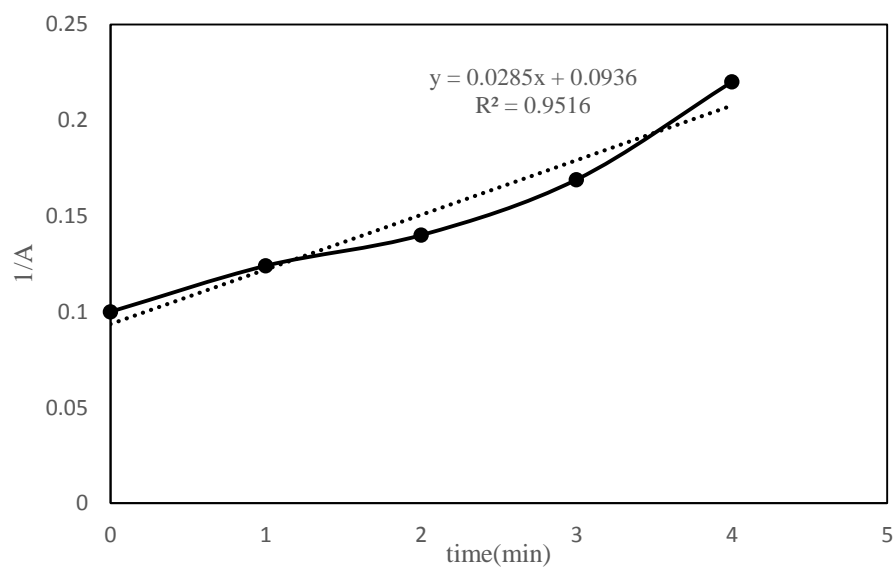


Fig. 4.7(b). 2nd order before 5 minutes

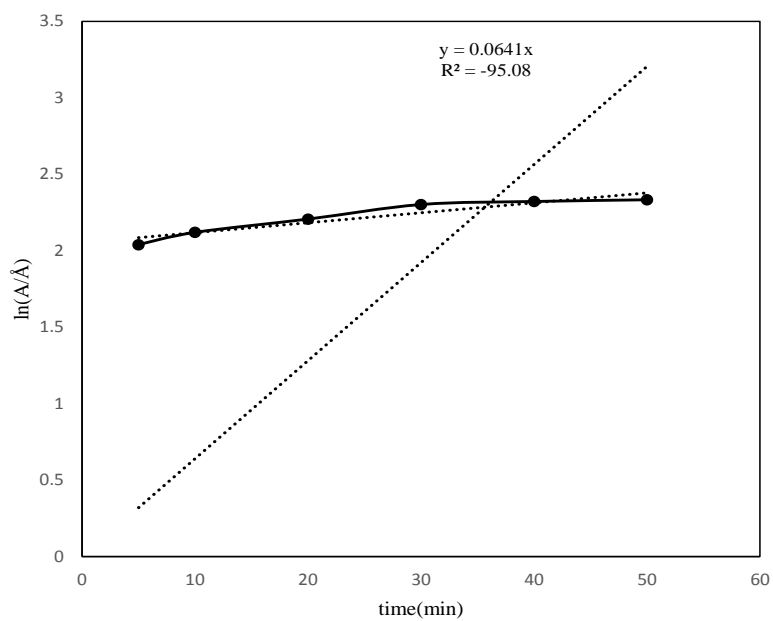


Fig. 4.7(c). 1st order after 5 minutes

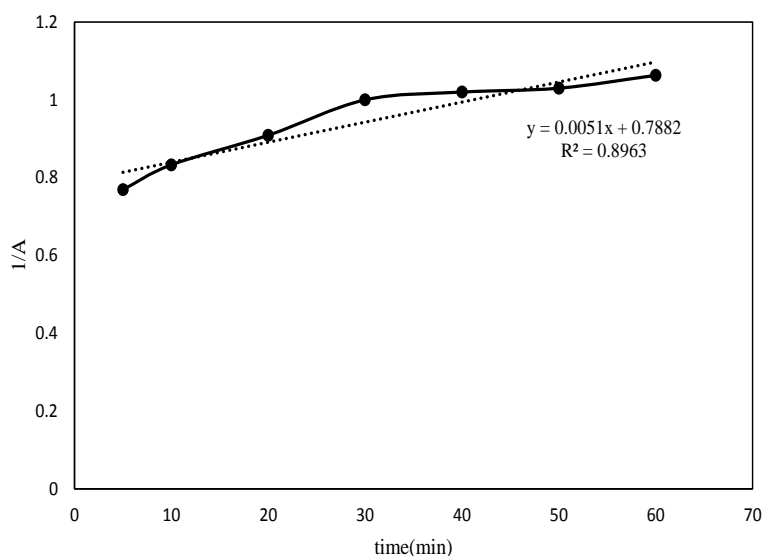


Fig. 4.7(d). 2nd order after 5 minutes

4.3.3. At 40^o C

Experiments were carried out at optimum conditions by maintaining the temperature at 40^o C. The experimental were plotted and formed that the dye degradation follows two step process. In first 5 minutes, the degradation rate was very higher but after 5 minutes, the rate of dye degradation was slower. Hence kinetic analysis was carried out in two stages, ie before 5 minutes and after 5 minutes. The results are shown in Fig 4.8.(a),(b),(c),(d). The R² values and rate constant values are tabulated in table 4.6.

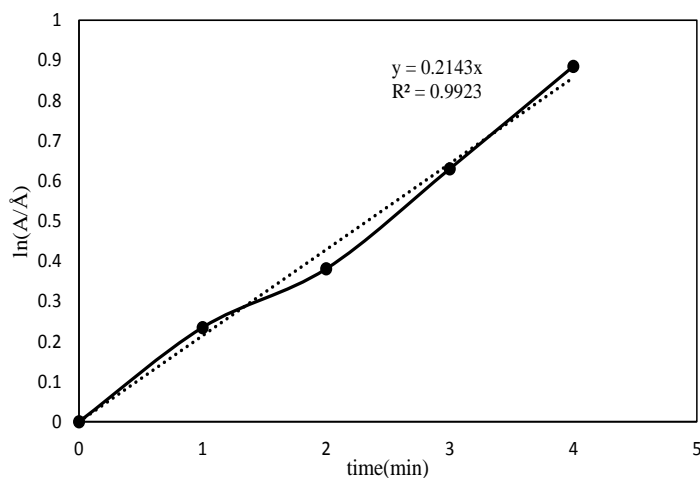


Fig. 4.8(a). 1st order before 5 minutes

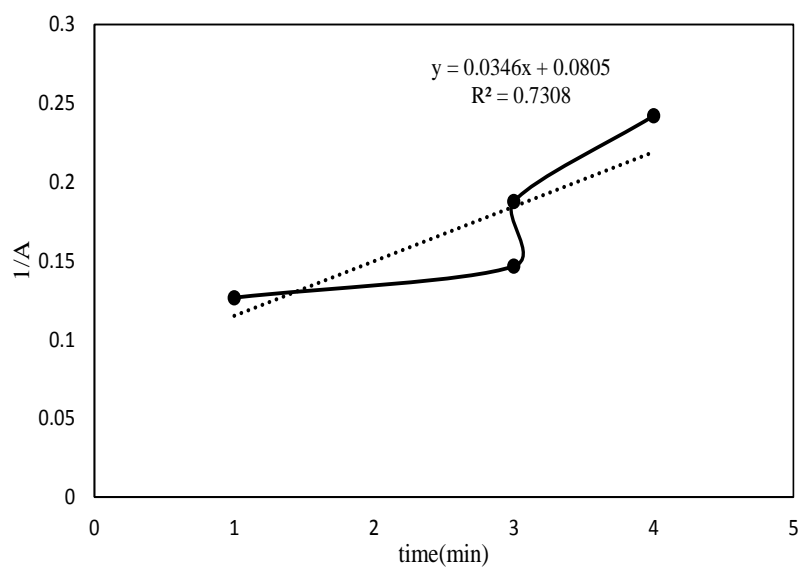


Fig. 4.8(b). 2nd order before 5 minutes

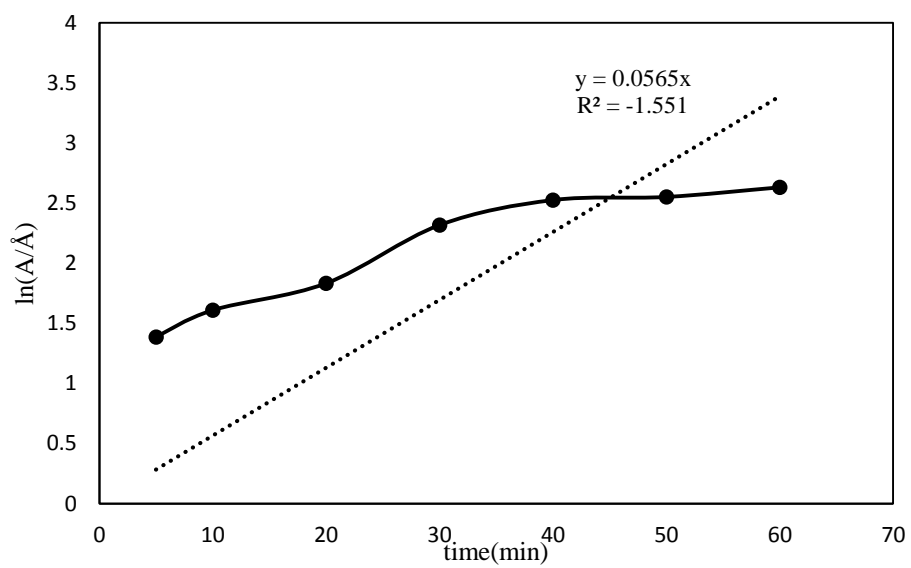


Fig. 4.8(c). 1st order after 5 minutes

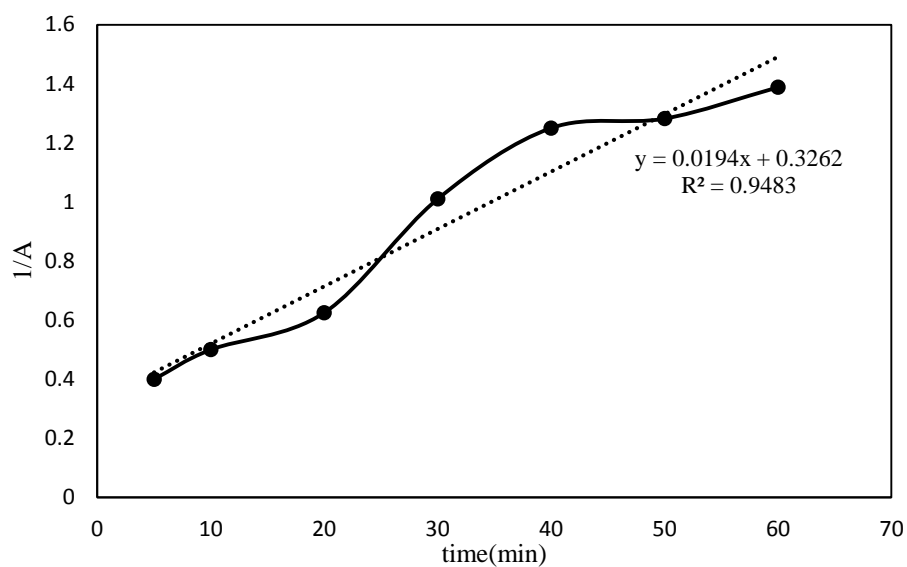


Fig. 4.8(d).2nd order after 5 minutes

From the graph R^2 values and k values are tabulated in Table 4.6. From the table it was observed that the Fenton process follows two step process. It follows 1st order process up to 5 minutes and follows 2nd order kinetics after 5 minutes.

Table 4.6. Rate constant values for Fenton process

temp(°C)	k	R^2	k	R^2	k	R^2	k	R^2
25	0.1685	0.9862	0.0247	0.9561	0.0463	-397.1	0.0012	0.9589
30	0.1883	0.9845	0.0285	0.9516	0.0641	-95.08	0.0051	0.8963
40	0.2143	0.9923	0.0346	0.7308	0.0565	-1.551	0.0194	0.9483

4.4. ACTIVATION ENERGY:

Arrhenius' equation gives the dependence of the rate constant, k of a chemical reaction on the absolute temperature, a pre-exponential factor and other constants of the reaction.

$$k = Ae^{-E_a/(RT)} \quad (4.1)$$

Taking the natural logarithm of Arrhenius' equation yields

$$\ln(k) = -E_a/R (1/T) + \ln(A) \quad (4.2)$$

Then, we plotted a graph of $\ln(k)$ vs $1/T$ to get the value of activation energy for 1st order kinetics (before 5 minutes) and 2nd order kinetics (after 5 minutes).

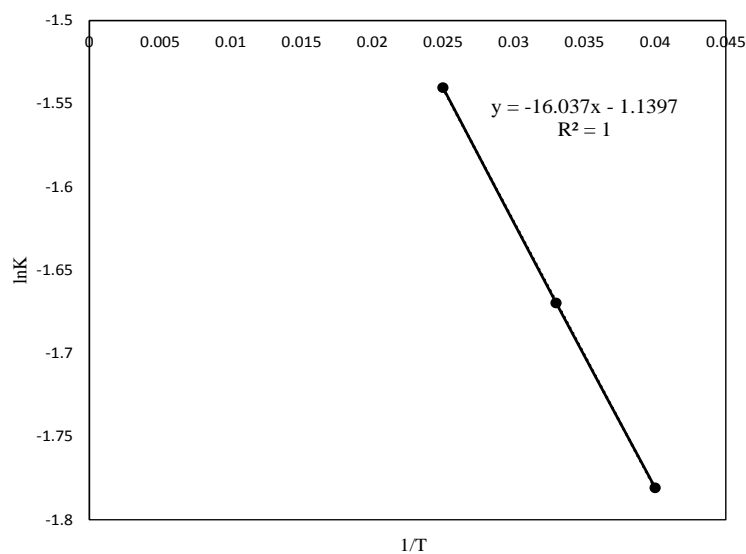


Fig. 4.9(a). 1st order before 5 minutes

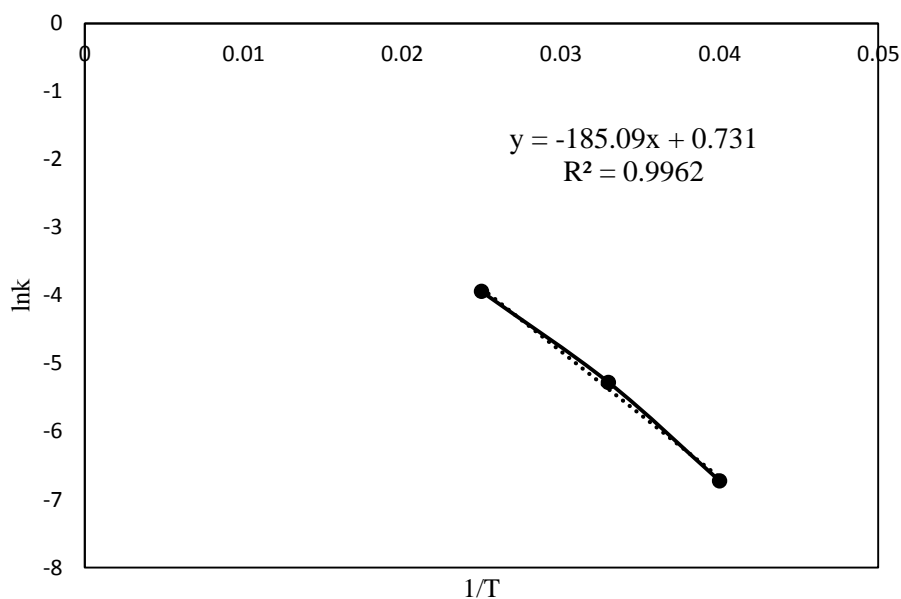


Fig.4.9 (b). 2nd order after 5 minutes

For 1st order, we get the E_a/R value from the slope of the graph i.e., 16.037.

We know, $R=8.314 \times 10^{-3} \text{ KJmol}^{-1} \text{ K}^{-1}$

So, $E_a = 36.399 \text{ KJmol}^{-1} \text{ C}^{-1}$. Hence Arrhenius Constant, $A= 0.319$

For 2nd order, we get the E_a/R value from the slope of the graph i.e., 185.09.

We know, $R=8.314 \times 10^{-3} \text{ KJmol}^{-1} \text{ K}^{-1}$

So, $E_a = 420.01 \text{ KJmol}^{-1} \text{ C}^{-1}$. Hence Arrhenius Constant, $A= 2.077$

4.5. GIBBS FREE ENERGY

After calculating the k values of reaction for 1st order and 2nd order reactions we calculate the Gibbs free energy which will tell us the spontaneity of the reaction i.e. whether the reaction is spontaneous at different temperatures or not.

Before 5 minutes it follows 1st order kinetics Table 4.6 so accordingly rate constant k is taken for calculating the ΔG° value. So by eq. 3.6 we observed {Table 4.7(a)}

Table 4.7(a) Gibbs free energy before 5 minutes

$\Delta G^\circ =$ gibbs free energy before 5mins		
temperature	$\ln k$	ΔG° (KJ)
25	-1.7808	96.917
30	-1.669	113.644
40	-1.54	139.81

After 5 minutes it follows 2nd order kinetics (see Table 4.6) so accordingly rate constant k is taken for calculating the ΔG° value. So by eq 3.6 we observed {Table 4.7(b)}

Table 4.7(b) Gibbs free energy after 5 minutes

$\Delta G^\circ =$ gibbs free energy after 5mins		
temperature	$\ln k$	ΔG° (KJ)
25	-6.725	381.597
30	-5.2785	359.421
40	-3.9428	357.962

By the results we infer that the reaction is highly non spontaneous since the ΔG° value is positive in all the cases.

4.6. MICROWAVE-FENTON PROCESS

To improve the process we enhance our process. So we introduced a microwave enhanced Fenton process to remove methylene blue from the solution. Since this is an extended version of Fenton's process, we performed the experiment with our optimised parameters (10ppm Dye, 30ppm Fe^{2+} , 100ppm H_2O_2 and 6pH).

The removal rate of methylene blue was increased and accelerated due to the assistance of microwave irradiation, fig 4.10 shows the difference in colour of dye solution before treatment and after the treatment of 5 minutes.



Fig. 4.10(a).Decolourisation of Methylene blue after Microwave-Fenton Process within 5 minutes

The experimental results are given in Table 4.8 and corresponding graph is shown in figure 4.10(b). From the results, it was observed that within 5 mins, 96% of dye was degraded and beyond that, there is no significant increase in degradation. On comparison with Fenton process, microwave Fenton process gave better results and quick degradation is possible provided energy consumption will be more. Hence this combined microwave Fenton process can be applied for higher concentration of dye solution.

Table 4.8. Percentage removal of dye for Microwave- Fenton Process

time(min)	% removal
0	0
5	95.8
10	96.2
20	96.3
30	96.4
40	96.42
50	96.8
60	97

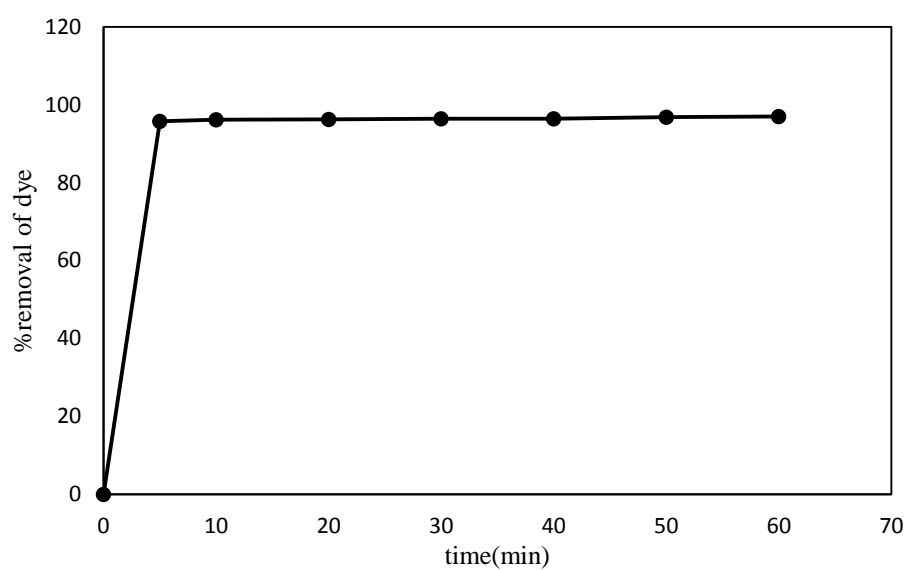


Fig. 4.10(b) Percentage removal of dye for Microwave-Fenton Process

CHAPTER 5

CONCLUSION

This project focuses on the application of Fenton process for the removal of methylene blue, a dye compound from water solution. Fenton process is powerful type of advance oxidation technique and it relies on the addition of iron (II) and H_2O_2 to create free radicals in the medium which causes effective degradation and removal of organic contaminants from wastewater. At optimum parameters conditions 96% removal of Methylene blue was obtained in 60 mins.

From the kinetics study, it was observed that the reaction follows 1st order kinetics for first 5 minutes, and then it follows 2nd order kinetics for the rest of the reaction period. Activation energy was found out to be positive, $36.399 \text{ KJmol}^{-1} \text{ C}^{-1}$ for first 5 minutes and $420.01 \text{ KJmol}^{-1} \text{ C}^{-1}$ after 5 minutes, which means the reaction is endothermic reaction.

Further the experiments were carried out using Microwave induced Fenton's Process, and the percentage removal was obtained within 5 minutes which is better than Fenton Process. Hence, it is inferred from the experiments that the most effective method is Microwave induced Fenton process for the removal of Methylene Blue.

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