

Oxidative Degradation of Methylene Blue Using Fenton Reagent

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Abstract— Methylene Blue dye is an aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$ and has some very distinctive uses in some fields like biology and chemistry. Its uses are diverse as they can be used in paper and pulp industries, leather industries and can also be used for medicinal purposes. This paper focuses on the degradation of methylene blue using Fenton and Oxidative processes and how to remove this dye compound from water solution. The material used, its environmental effect, advantages and recommendations are also discussed.

Index Terms— Degradation, Dye, Hydrogen Peroxide, Fenton, Methylene Blue.



1 INTRODUCTION

Textile industries produce enormous wastes involving various dyes and they are found to have presented serious environmental problems due to the fact that dyes are highly coloured and designed to resist chemical, biochemical and photochemical degradation. 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. Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediates manufacturing industries, textile units, paper making industries, pharmaceuticals, cosmetics ,synthetic and manufactured detergents, and tanneries are the typical industries that discharge toxic and poisonous organic compounds at low concentrations to the nearer and closer water bodies, thus making the water polluted and undesirable. It is important and necessary to develop and create novel and cost-effective technologies to treat this wastewater.

1.2 ENVIRONMENTAL FATE

An aggregate of 15% of the world production of dyes is lost during dyeing process and its discharged in textile and fabric effluents (Zollinger, 1991). Frequent users of some these chemicals include paper and pulp manufacturing industries, dyeing of cloth, leather treatment and printing. Most of the solutions being used contain dyes which are released as effluents (Bukallah et al., 2007).The release of coloured wastes into streams does not only affects the aesthetic nature, but this coloured wastes also hinders the transmission of sunlight into streams and therefore slows down photosynthetic activities (Namasivayam et al., 2001). Several methods have been tested for dye removal from the industrial effluents to lessen their impact on the environs. Some of these methods are adsorption which includes organic or inorganic matrices, chemical precipitation, coagulation and electro coagulation. (Lata et al., 2008; Gong et al., 2008; Cheng et al., 2008; Augustine, 2008; Rauf et al., 2008; Xiaofei and Khalil, 2008; Daneshvar et al., 2003) Recent findings on the development of chemical treatment of wastewater have resulted in great improvement in the oxidative decolourisation of organic compounds dissolved in aqueous media.

2 LITERATURE REVIEW

2.1 METHYLENE BLUE

Methylene Blue is a heterocyclic chemical compound which is aromatic in nature and its molecular formula is $C_{16}H_{18}N_3S^+Cl^-$. It is a compound that is very important because of its various uses in unique areas, these areas include biology and chemistry. Methylene blue emerges as a solid, odourless, dark green powder which gives a blue solution when dissolved in water at normal room temperature. The structural form when hydrated has 3 molecules of water per molecule of methylene blue and this particular compound should not be confused with methyl blue nor with the methyl violets which are mostly used as pH indicators. Methylene blue was prepared first in 1876 by a German chemist Heinrich Caro (1834-1910). The compound was set up by treating 4-aminodimethylaniline with hydrogen sulphide which is dissolved in hydrochloric acid (HCl), after which oxidation with ferric chloride was done.

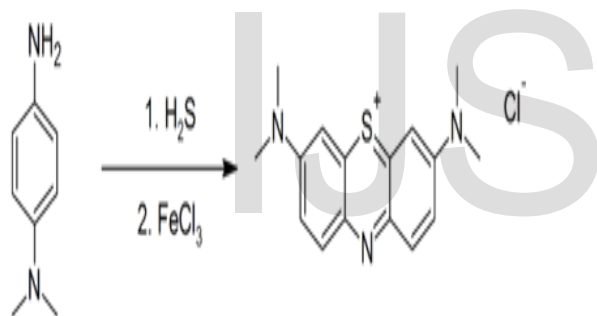


Figure 1 preparation of methylene blue

Methylene blue is a very potent and strong cationic dye which absorbs light maximally around 670nm. This absorption rate depends on many factors which include protonation and adsorption, to other materials.

Table 1: Absorption of Methylene Blue

Species	Absorption peak	Extinction coefficient ($dm^3/mole \cdot cm$)
MB^+ (solution)	664	95000
MBH_2^+ (solution)	741	76000
$(MB^+)_2$ (solution)	605	132000
$(MB^+)_3$ (solution)	580	110000
MB^+ (adsorbed on clay)	673	116000
MBH_2^+ (adsorbed on clay)	763	86000
$(MB^+)_2$ (adsorbed on clay)	596	80000
$(MB^+)_3$ (adsorbed on clay)	570	114000

2.2 USES OF METHYLENE BLUE

Methylene blue is primarily a basic dye widely utilized for coloring, printing cotton and silk etc. It is likewise useful for medicinal purposes because of its antiseptic properties. It can also be used by paper and pulp manufacturers, it can also be used in the treatment of leather.

2.3 AN INDICATOR

Methylene blue can also be used as a pointer to verify if eukaryotic cells like yeast are dead or alive. Methylene blue cannot enter and penetrate viable cells when they are alive leaving them unstained. However, if the cells are dead methylene blue will penetrate the cell membrane staining and making the cells blue. Respiration of yeast can be controlled by methylene blue when it picks up hydrogen ions made during this process therefore preventing the yeast cell from using those ions to release energy.

2.4 METHYLENE BLUE IN CHEMISTRY

Methylene blue is widely used as a redox indicator in chemistry mostly analytical chemistry, it's a pointer that indicates the presence or absence of oxygen. Oxygen-rich environments are said to be oxidizing. Some chemical elements, such as oxygen have very strong affinity for electrons in which they can strip electrons away from the atoms of other

elements these are known as oxidizing agents. Methylene blue indicates the presence of oxidizing agents because it is oxidized by these compounds. When electrons are stripped from methylene blue, the molecule gives a blue colouration to the solution showing us a clear sign of a chemical change. Volumetric analysis, makes reaction between Fehling's solution and reducing sugars more visible using methylene blue which are also reagents in redox titrations.

This paper discusses the effectiveness of Fe^{2+} and H_2O_2 towards oxidative degradation of dye. The initial rate of the degradation of the dye as a function of concentrations of dye, Fe^{2+} and H_2O_2 will likewise be reported and accounted for

2.5 OXIDATIVE PROCESSES

This is a procedure in which oxygen is created and caused to combine with other molecules. The oxygen may be used as elemental oxygen, as in air, or in the form of an oxygen-containing molecule which is able to give up all or part of its oxygen. Most oxidations occur with the release of a lot of energy in the form of either heat, power, light or electricity. The extreme effect of oxidation are oxides of the elements involved. These oxidations occur naturally as corrosion, decay and decomposition where by smouldering and burning of matter such as wood, petroleum, and sulphur are used as oxides of the basic and essential elements.

The key variables to be considered in any partial oxidation are temperature, pressure, mole ratio of oxidising agent to know whether the substance to be oxidized is to be kept in the liquid or vapour phase, nature of catalyst and reaction time. Only a narrow range of conditions distinctive to each substance being oxidized and each product required will give a reasonable yields.

2.6 FENTON PROCESS

H.J.H. Fenton in 1894 discovered Fenton reaction and he stated that Hydrogen peroxide (H_2O_2) could be triggered by ferrous salts (Fe^{2+}) to oxidize tartaric acid. More than 1700 rate constants for OH reactions with organic and inorganic compounds in aqueous solution have been reported in the past few decades there by bringing to lime light the importance of OH reactions. Related reactions with Fenton include Hydrogen peroxide (H_2O_2) reacting with iron ions to create active oxygen species that oxidize inorganic or organic compounds. In recent past, Fenton reaction was effectively

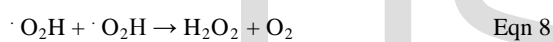
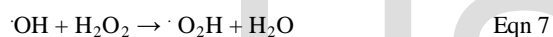
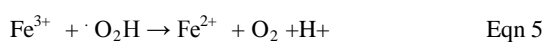
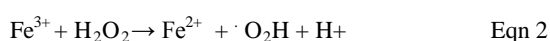
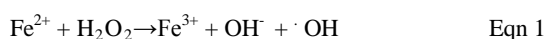
utilised in the treatment of wastewater process for the removal of harmful organics from wastewater. The traditionally recognized Fenton mechanism is shown below by Eqns. (1)–(9) and its reaction rates were well and correctly reported. Eqn. (1) is recognized as Fenton reaction and this signifies the oxidation of ferrous to ferric ions to degrade H_2O_2 into hydroxyl radicals. It is generally known as the core of the Fenton chemistry. Moreover, other reactions must be looked into so as to comprehend and understand the entire process. The produced ferric ions can be slowed down by reacting with more hydrogen peroxide to produce again ferrous ion and more or excess radicals as shown in Eqn. (2). This reaction is called Fenton-like reaction which is much slower than Fenton reaction, and allows ferrous salt (Fe^{2+}) to be regenerated in an efficient cyclic mechanism. In Fenton like reaction, aside from ferrous ion regeneration, hydro-peroxyl radicals ($\cdot O_2H$) are formed. The hydro-peroxyl radicals in like manner may attack organic pollutants, but hydroxyl radicals are less sensitive to it. However, it should also be noted that the iron added in small amount acts as a catalyst while H_2O_2 is continuously used up to produce and generate hydroxyl radicals. Eqns. (2)–(5) characterize the rate limiting steps in the Fenton chemistry since hydrogen peroxide is consumed and ferrous iron is recovered from ferric ion through these reactions.

Furthermore Eqns (6)–(9) was said to have occurred during the Fenton process and they are radical–radical reactions or hydrogen peroxide–radical reaction. Breaking down of hydrogen peroxide to molecular oxygen and water occurs In the presence or absence of any organic molecule to be oxidized as shown in Eqn. (10). This reaction lead to abuse of bulk oxidant and thus an unnecessary raise on treatment cost. Eqns. (1)–(9) shows that the Fenton process follows a complex mechanism. The chain initiation reaction activates the occurrence of the creation of desired hydroxyl radical however hydroxyl radicals can be poached by ferrous ions (Eqn. (3)), hydrogen peroxide (Eq. (7)), hydro-peroxyl radicals (Eqn. (9), and/or even may be auto scavenged

(Eqn. (6)). The foregoing analysis shows that hydrogen peroxide (H_2O_2) may act both as radical generator (Eq. (1)) and as scavenger (Eqn. (7)). Hydroxyl radicals may attack organic radicals generated by organics present in the wastewater. Those radicals react with ferrous and ferric ions, as indicated in the equations below. Fenton process can occur out at room temperature and atmospheric pressure. Further more, reagents needed are readily available and they are easy to store and handle, it is safe and

they do not cause any damage to the environment. However, two major impediments have been identified. The first is the wastage of oxidants because the radical scavenging effect of hydrogen peroxide (Eq. (7)) and it decomposing itself (Eq. (10)). The second refers to the formation of solid sludge and the continuous loss of iron ions.

Quite a number of economic and environmental hindrances have been said to occur with Fenton sludge however, innovations allowing an efficient use of hydrogen peroxide (H₂O₂) have to be researched. Furthermore, efforts must be made for the regeneration and recovery of iron ions and their subsequent recycle and reuse.



MATERIALS AND METHODS

3.1 MATERIALS AND CHEMICALS

Methylene blue, FeSO₄·7H₂O (B.D.H.), H₂O₂(35% w/v), HCl, NaOH, are all purchased from E. Merck, A.R. or G.R. grades and used as received without any further purification All solutions were made in distilled water.

3.2 METHODS

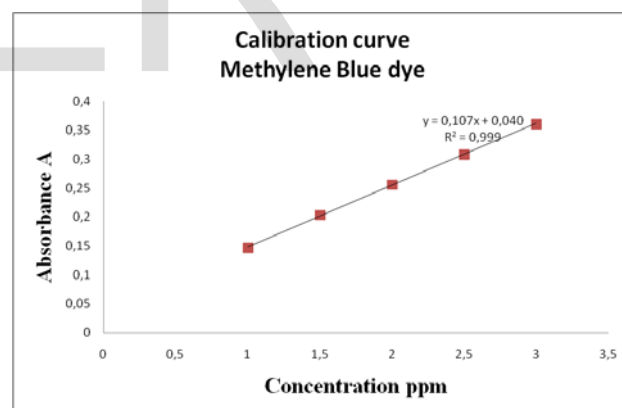
3.2.1 STOCK SOLUTIONS PREPARATION

50 ppm of dye stock solution were prepared weighing 0.05g methylene blue and diluting it with distilled water to 100ml Likewise 0.993g of FeSO₄·7H₂O and 1.52ml of Hydrogen peroxide (H₂O₂) was also prepared in deionised water and diluted up to 100ml

3.2.2 CONCENTRATION MEASUREMENT

A calibration curve is a method of determining the concentration of a substance in an unknown sample by comparing the unknown with the set of known concentration which shows how the system response to analytical signal that changes with the change in the concentration of the analyte (the substance to be measured) which is dye in this study.

A series of dye stock concentration were prepared to get 1ppm, 1.5ppm, 2ppm, 2.5ppm, 3ppm which are within the ranges of concentrations to be analysed in the unknown samples and are used to get the calibration points as shown in the figure below



Formula to calculate concentrations $x = (y - 0.04) / 0.107$

$x = \text{conc}$

$y = \text{absorbance}$

Figure 2 An image of calibration curve used

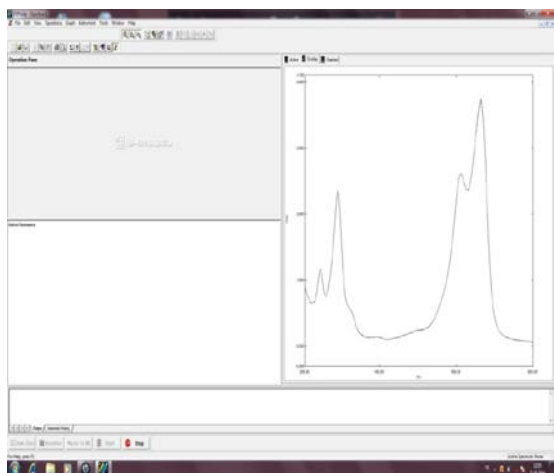


Figure 3: Spectrophotometric view of mb calibration curve

3.2.3 PH ADJUSTMENT

The adjustment of pH on methylene blue dye was examined with the pH meter ranging from 2.0 to 4 and it appears that the best pH for the decolourisation of all dyes observed were in the range between 3 and 4. The pH of the solutions was adjusted using NaOH and HCL. The optimization of the pH was carried out at 300C, and the volume of each reaction was 100ml. The water bath was at 120 rpm to stir the solution and samples were collected at intervals and measured with UV- VIS Spectrophotometer. The oxidative degradation process was measured using the equation;

$$= (C_0 - C_t) / C_0$$

Where C_0 and C_t (ppm) are the initial concentration and final concentration at time t respectively,

3.3.5 ANALYTICAL INSTRUMENTS

3.2.6 ULTRAVIOLET AND VISIBLE ABSORPTION SPECTROSCOPY (UV-Vis)

Ultraviolet and Visible absorption spectroscopy (UV-Vis) measures the reduction of a beam of light after passing through a sample or reflection from a sample surface. Absorption measurements is one which can be at a single wavelength or an extended spectral range. Ultraviolet and visible light are active and strong enough to enhance outer electrons to high energy levels.

UV-Vis spectroscopy is mostly useful to inorganic complexes or molecules in solution. The UV-Vis spectra have diverse characters that are of limited use for sample recognition but very useful in quantitative measurements. Concentration of analytes in solution can be known by applying the Beer Lambert Law and measuring the absorbance at a given wavelength. The Beer Lambert Law can be written as $A = \epsilon * L * C$ where ϵ is the adsorbitivity coefficient, L is the path length C is a constant and A is the concentration. Since the UV-Vis range covers the range of human visual prowess of about 400 - 750 nm, UV-Vis spectroscopy is helpful in characterising the absorption, reflectivity, and transmission of a variety of technologically essential materials, such as pigments, coatings, and filters. There are more qualitative functions that generally entails recording a portion of the UV-Vis spectrum for characterization of the optical and electronic properties of materials.

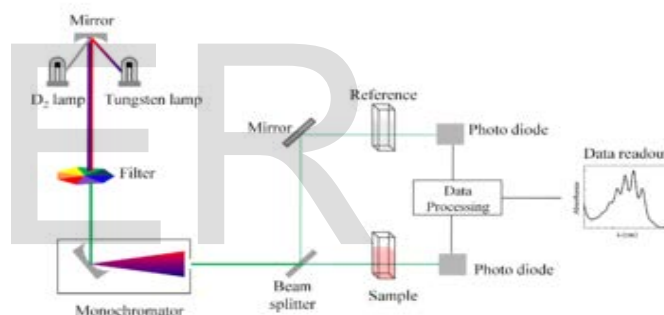


Figure 4 Schematic view of a dual-beam UV-vis spectrophotometer



Figure 5 Pictures of dual-beam uv-vis spectrophotometers

3.2.7 PH METER

A digital pH-meter WTW series pH 720 pH meters was used to measure the pH of methylene blue. NaOH, HCL, were acid and base used in the regulation of the pH of the solution



Figure 6 pH meter

3.2.8 WATER BATH

The water bath used was GFL 1083 and samples were taken at various resolutions per minutes, at a constant temperature of 30 degree at 120rpm. This allowed for temperature regulation and prevent the settling of the methylene blue



Figure 7 Water Bath

ULTRASONIC BATH



Figure 8: Ultrasonic Bath

These ultrasonic baths or cleaners have big transducer tanks which creates a high-powered ultrasonic intensity throughout the entire oscillating tank. Steady power and automatic frequency control guarantees optimum distribution and circulation of ultrasonic energy. Many a times it is used for perfect mixing of some substances or chemicals in the laboratory as the case may be

ANALYTICAL BALANCE

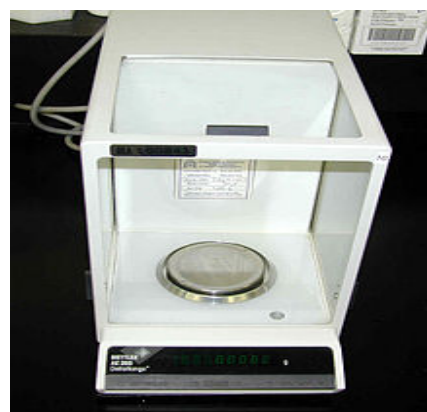


Figure 9 :Analytical Balance

An analytical balance is a class of balance designed to measure small mass of substance in the sub-milligram range. The measuring plate of an analytical balance is inside a transparent area with doors to keep out dust and to make sure it does not collect any air currents in the room because it may have an effect on the operation of the balance. This transparent area that is

enclosed is called a draft shield. The use of a mechanically vented balance safety area, which has distinctively designed acrylic airfoils, permits a smooth turbulence-free airflow that prevents balance fluctuation. Analytical balance measures mass up to as low as 0.1 mg or better still it measures down to 1µg without fluctuations or loss of product. Also, the sample to be measured must be at room temperature to prevent natural convection from forming air currents inside the enclosure causing an error when taking readings. A single pan mechanical substitution balances maintains and keep consistent response throughout the operation. Useful capacity can be achieved by keeping a constant load on the balance beam

CHAPTER 4

4.1 RESULT AND DISCUSSION

In this chapter the results of varying all the parameters used in the oxidation of dye using Fenton reaction are going to be discussed. The effect of temperature, pH, and Fe and H₂O₂ will be discussed individually.

4.2 AOP EXPERIMENTS

Of all the advanced oxidation processes, the Fenton-like oxidation process was selected as it is advantageous over other technologies to degrade a wide variety of hazardous organics and also this treatment is quite cost-effective. The Fe²⁺/H₂O₂ oxidation has been studied for aqueous dye solutions having dye concentration in the range (10ppm - 30ppm) The concentrations of Fe²⁺ and H₂O₂ were varied in the range from (1ppm - 4ppm) and (50 - 200ppm), respectively.

4.3 FIRST ORDER REACTION

First Order Reaction is a reaction that depends on the concentration of only one reactant. Mathematically it can be written as $C=C_i \cdot \exp(-k \cdot t)$

T = Time

C = The concentration of the reactant

C_i = The initial concentration of reactant

K = Reaction rate constant which is usually described as the Arrhenius equation

R = The universal gas constant

4.4 EFFECT OF PH

The effect of pH on the degradation or removal of pollutant is one of the most important parameters. pH plays a vital role on the degradation or removal of dye and as the percentage may increase or decrease with increasing pH or vice versa. The removal of dye was carried in the pH range of 2 to 4.

HCl and NaOH was used to adjust the pH respectively and pH 3 was used as the working range for this experiment at 30°C with the dye concentration set at 10ppm, Fe²⁺ at 1ppm and H₂O₂ at 100ppm which were the optimum values. The effect of pH on the degradation of dye is shown below and it can be seen that as the pH increases with time the rate of removal or degradation was also faster and the colour of dye disappears very rapidly given below are the result

TIME(min)	0,00	2,00	4,00	8,00	10,00	15,00	18,00	20,00	25,00	30,00
pH 2	100,00	65,00	35,00	30,00	29,00	27,00	25,50	24,00	20,00	17,50
pH 3	100,00	91,67	16,67	6,67	6,00	5,33	4,50	3,83	3,50	3,00
pH 4	100,00	75,00	40,25	19,75	12,75	8,00	7,00	6,25	5,00	3,75

Table 2: A Table Showing Time and Ph

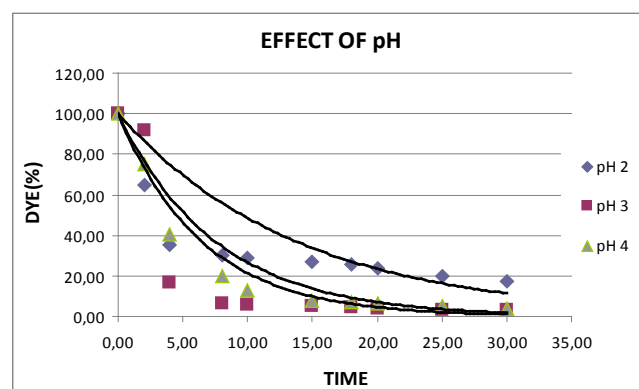


Figure 10: A graph showing the effect of pH(experimental conditions include 30°C temperature, 10ppm dye, 100ppm H₂O₂ and 1ppm Fe²⁺)

4.5 EFFECT OF TEMPERATURE ON DYE

Experiments were conducted at four different temperatures between 30oC and 60oC under uniform conditions to examine the effect of temperature on the degradation of aqueous dye solutions. The results below shows that there is a substantial increase in the extent of degradation of the dye when the reaction temperature was raised from 30oC to 45oC. A further increase in the reaction temperature from 45 to 50oC resulted in the increase in the extent of degradation of the dye. Moreover, there was further increase in the rate and extent of degradation of the reaction in the temperature between 50 and 60oC. At higher reaction temperatures, the thermal disintegration of the hydrogen peroxide resulted in the slowing down of its effective concentration towards

making hydroxyl radicals, and this is most likely the reason behind lower conversion of the dye at high reaction temperatures.

Time (Minutes)	0,00	2,00	4,00	8,00	10,00	15,00	18,00	20,00	25,00	30,00
Temp at 30oC	100,00	97,14	89,29	79,14	72,86	58,14	50,00	42,86	27,86	17,43
Temp at 45oC	100,00	98,46	80,15	54,62	42,00	22,00	15,23	12,15	8,00	6,31
Temp at 50oC	100,00	84,00	18,40	15,60	14,80	14,00	13,20	12,00	10,00	8,80
Temp at 60oC	100,00	70,00	55,00	34,00	30,00	25,00	22,00	21,00	18,00	15,00

Table 3: A Table Showing Temperature and Time

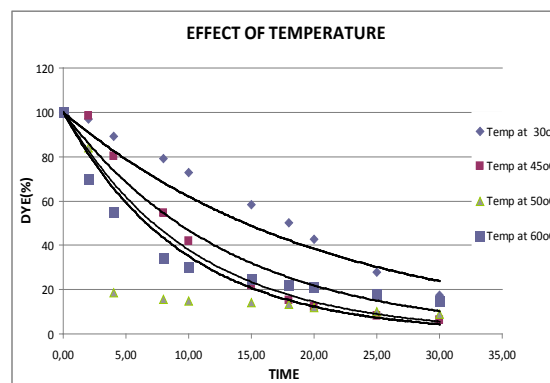
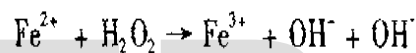


Figure 11: A graph showing the effect of temperature (experimental conditions include pH 3, 10ppm dye, 100ppm H2O2 and 1ppm Fe2+)

4.6 EFFECT OF IRON (Fe)

Fenton chemistry is a well known and its one of the high potential oxidation technologies because it produces a highly reactive specie {OH-}(Fenton 1894; Haber 1934.). Following the equation of the reaction below,



degradation of methylene blue using fenton is being investigated. its is also clear from the equation above that degradation of methylene blue not only follow this reaction but other reaction also play important roles in the degradation. Degradation of methylene blue occurred within 30minutes using fenton process and the degradation of dye was gradual which means the oxidant specie OH which was responsible for the degradation was generated continuously. It was also observed that there was no precipitation of iron hydroxide at the end of the degradation. Addition of Fe alone to the dye solution in the absence of H2O2 was found to have no measurable effect on the oxidation of dye neither was there any change in the degradation or removal of colour in the dye. Therefore it can be said that there is a gradual degradation of dye using Fenton reaction. It was also found out from literature that fenton process works best with the range between 1 and 4. Optimisation was done using four different concentrations which ranges from 1 - 4 mg/l(1, 2, 3 and 4 mg/l) Fe (II) was used to find the optimum dose of Fe(II) for Fenton process. In

order to achieve this Dye and H₂O₂ concentrations was kept constant at 10ppm and

concentration in ppm	K	R ²
1	0.17	0.989
2	0.2	0.959
3	0.2	0.941
4	0.28	0.675

100ppm respectively, Result were given in the graph below. 1mg/1 of Fe(II) was chosen because faster elimination occurred at this dosage and dye was degraded completely at 30minutes. Looking at the graph below we can see a considerable trend in the degradation of dye from 9.91 to 0.05ppm that is as the time increase the removal or the rate of degradation of dye increase and from the exponential graph below we could also see the R₂ of the graph to be 0.98 therefore as time increases the rate of removal is faster and there was 99% removal this percentage was determined using the equation % Removal = (C₀-C_f)/C₀ Where C₀ and C_f

Time	0,00	2,00	4,00	8,00	10,00	15,00	18,00	20,00	25,00	30,00
Effect of Fe ²⁺ removal(1ppm)	100	56,1	45,41	29,57	22	9,69	5,55	3,63	1,21	0,5
Effect of Fe ²⁺ removal(2ppm)	100	54,79	44,6	36,73	24,52	18,37	5,55	3,53	1,41	1,21
Effect of Fe ²⁺ removal(3ppm)	100	67	48,34	13,72	4,54	3,63	2,52	1,31	1,01	1,01
Effect of Fe ²⁺ removal(4ppm)	100	46,42	26,84	4,74	3,33	2,32	1,51	1,21	1,11	1,01

(ppm) are the initial concentration and final concentration at time t respectively, At the end of 30 minutes, 1mg/1 of FeSO₄.7H₂O degraded 10ppm of dye methylene blue and 100pm of H₂O₂ Hydrogen peroxide with 99% removal

Table 4: A Table Showing The Effect Of Fe On The Degradation Dye

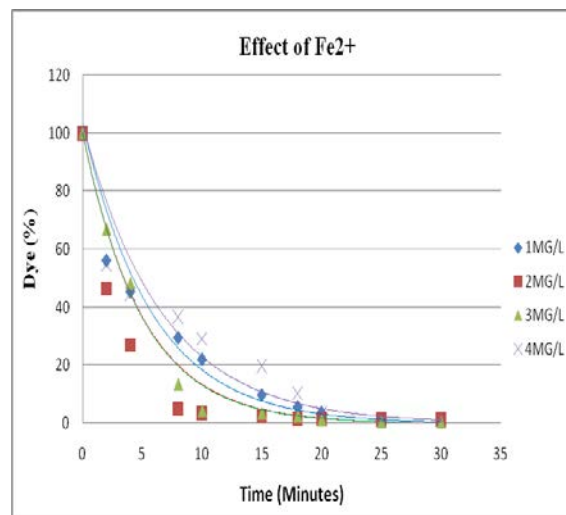


Figure 12: A graph showing the exponential effect of Fe on the degradation of dye

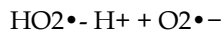
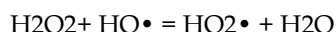
Table 5: A Table showing the conc(ppm) K and R₂

4.7 EFFECT OF H₂O₂ ON DYE DEGRADATION

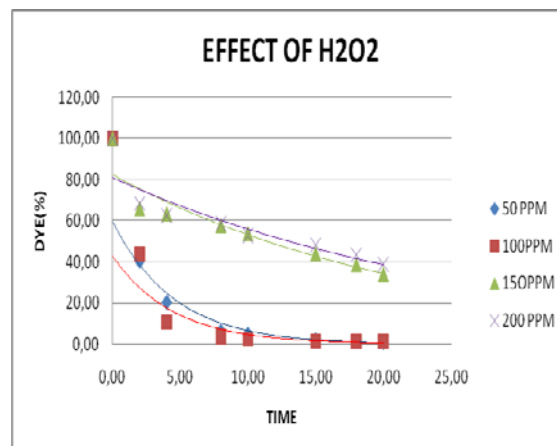
In order to investigate the effect of H₂O₂ concentration on the degradation kinetics, experiments was conducted at different H₂O₂ concentrations. The H₂O₂ concentration was varied from 50ppm – 200 ppm at a fixed Fe²⁺ concentration of 1ppm and dye concentration of 10ppm the H₂O₂ concentration of 100ppm was effective in degrading about 99% of dye in 20 minutes at 30°C temperature. 100ppm was selected as optimum H₂O₂ concentration that is efficient for the degradation of the dye. The selection of this optimum concentration is important from the commercial point of view (due to the cost of H₂O₂). De et al. H₂O₂ concentration for the breaking down of methylene blue by Fenton’s reagent could be explained as follows. At low H₂O₂ concentration, the HO• radicals preferentially attack the benzene ring of the organic contaminant present in water. At high H₂O₂ concentration however, there is a competition between the substrate and H₂O₂; in

other words, H₂O₂ in high concentration acts as a scavenger of the highly potent HO• radicals to produce per hydroxyl radical, HO₂•

Overall efficacy of Fe²⁺ / H₂O₂ is thus found to be low at relatively higher H₂O₂ concentrations.



Looking at the table below it could be seen that there was effective removal of dye as time increase at 20 minutes with H₂O₂ and the percentage removal was calculated using the equation $\% \text{ Removal} = (C_0 - C_f) / C_0$ Where C₀ and C_f (ppm) are the initial concentration and final concentration at time t respectively, and 99% removal was achieved and the exponential effect was also analysed and the R² was seen to be at 0.96 all results and tables were given below as analysed



Time	0	2	4	8	10	15	18	20	25	30
Conc of dye10 (ppm)	100	80,7	60,5	36,7	28,4	5,4	3,5	2,6	1,6	0,9
Conc of dye15 (ppm)	100	78,8	65,7	43,6	33,2	14,7	4,7	2,8	2,4	2,2
Conc of dye20 (ppm)	100	55,8	39,6	19,8	11,6	5,0	3,0	2,3	1,8	1,6
Conc of dye25 (ppm)	100	56,7	39,9	24,0	19,4	6,4	3,4	2,8	2,4	2,3
Conc of dye30 (ppm)	100	53,2	33,0	16,7	11,8	3,7	3,0	2,8	2,6	2,5

Figure 13: Exponential Effective Degradation of 10mg/l of Mb under Various H₂O₂ Dosages and 1mg/L of Fe(II)

Table 6: A table showing the concentration of dye and H₂O₂ with Time

0	2	4	8	10	15	18	20
concentration in ppm	40,36	20,48	6,56	5,05	1,51	0,86	
50			0.04		0.919		
100	43,39	10,39	3,21	2,12	0,964	1,01	0,91
150			0.03		0.879		
100,00	65,79	63,27	57,52	53,78	43,90	38,65	33,91
200			0.22		0.875		
100,00	68,42	62,26	58,53	52,77	48,13	43,39	38,65

Table 7: A Table Showing the Exponential Effect of H₂O₂ with its Concentration, K values and R

4.8 EFFECT OF INITIAL DYE CONCENTRATION

The influence of various initial dye concentrations on decolourisation efficiency was investigated and the optimum dye concentration was determined. Concentrations of dye solution having 10ppm, 15ppm, 20ppm, 25ppm and 30ppm were separately treated with Fenton reagent solutions and 10ppm was taken as the optimum concentration because there was 99% of removal as shown below

The result from the graph below shows that there is increase exponentially with time. Therefore it can be seen that there is consistent degradation of dye as the time increases. From the table below the time was taken from 0 to 30 minutes and there was a considerate degradation in the absorbance with time as the time increases.

Using the equation

$$\% \text{ Removal} = (C_0 - C_t) / C_0$$

Where C₀ and C_t (ppm) are the initial concentration and final concentration at time t respectively, 99% removal was achieved using the values from the table above therefore we conclude that there was efficient removal of dye after 30 minutes. The exponential effect was also analysed and the result is also given below with its

$$R^2 = 0.96$$

Table 8: A table showing the concentration of dye and time

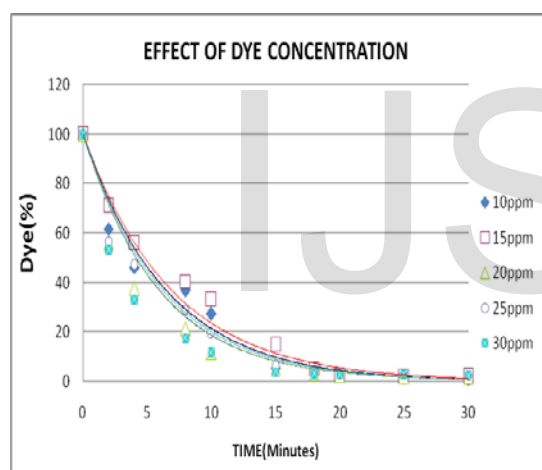


Figure 14: Effect of the exponential effect of dye

Table 9: Table showing the conc(ppm) K and R2

concentration in ppm	K	R2
10	0.16	0.968
15	0.14	0.943
20	0.16	0.905
25	0.15	0.904
30	0.16	0.798

The removal of methylene blue was investigated under the following parameters: Effect of pH, Fe²⁺ dose, temperature, and H₂O₂ concentration. Experiments were carried out with different

initial dye concentrations (10, 15, 20, 25 and 30 ppms) and it was found that degradation efficiency was maximum at 10ppm. The iron dosage was set to 1mg/l after optimizing with (1, 2, 3, and 4 mg/l). The Degradation of methylene blue occurred within 30minutes using fenton process and the degradation of dye was gradual which means the oxidant specie OH which was responsible for the degradation was generated continuously. It was also observed that there was no precipitation of iron hydroxide at the end of the degradation. Similarly, concentration range at of H₂O₂ (hydrogen peroxide) addition was optimised using (50, 100, 150, and 200 mg/l) and 100 mg/l was selected as an optimum value where maximum dye removal was observed

Concentration measurement of dye was done by using visible spectrophotometer at 650nm wavelength. Experiments on temperature were conducted at four different temperatures between 30oC and 60oC under uniform conditions to examine the effect of temperature on the degradation of aqueous dye solutions The result shows that there is substantial increase in the extent of degradation of the dye when the reaction temperature was raised from 30oC to 45oC. A further increase in the reaction temperature from 45 to 50oC resulted in the increase in the extent of degradation of the dye. Moreover, there was further increase in the rate and extent of degradation of the reaction in the temperature between 50°C and 60°C.

At higher reaction temperatures, the thermal disintegration of the hydrogen peroxide (H₂O₂) resulted in the slowing down of its effective concentration towards making hydroxyl radicals, and this is most likely the reason behind lower conversion of the dye at high reaction temperatures.

At 30 degrees it there was a linear increase and there was a decrease exponentially from 45 to 60 degrees respectively. The effect of pH on the degradation or removal of pollutant was also considered as is one of the most important parameters and pH plays a vital role on the degradation or removal of dye and as the percentage may increase or decreases with increasing ph or vice versa. The removal of dye was carried in the pH range of 2 to 4. HCl and NaOH was used to adjust the pH respectively and pH 3 was used as the working range for this experiment at 30oC with the dye concentration set at 10ppm, Fe²⁺ at 1ppm and H₂O₂ at 100ppm which were the optimum value. Optimum pH was found to be 3.0 where by 99% removal of dye was achieved within 30 minutes

CONCLUSIONS

This work 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 H₂O₂ (hydrogen peroxide) to create free radicals in the medium which causes effective removal of organic contaminants. It is therefore recommended that further studies should be conducted to see the removal of TOC and the remaining toxic effects of the resulting solution.

[11] Xiaofei, X., Khalil, H., 2008. J. Hazard. Mater. 166, 407-414.

[12] Zollinger, H., 1991. Color Chemistry Synthesis, Properties and Applications of Chemistry and Pigments, second ed. VCH, Weinheim.

REFERENCE

[1] Augustine, E.O., 2008. Biochem. Eng. J. 40, 8-18.

[2] Bukallah, S.B., Rauf, M.A., Alali, S.S., 2007. Dyes Pigments 74, 85-87. chemical biodegradability, Water Res. 35 (2001) 1047-1051.

[3] Cheng, W., Wang, S., Lu, L., Gong, W., Liu, X., Gao, B., Zhang, H., 2008. Biochem. Eng. J. 39, 538-546. comparison among photocatalysis, Fenton and photo-Fenton processes

[4] Daneshvar, N., Ashassi-Sorkhabi, H., Tizpar, A., 2003. Sep. Purif.

[5] Gong, R., Sun, J., Zhang, D., Zhang, K., Zhong, K., Zhu, G., 2008. Bioresour. Technol. 99, 4510-4514.

[6] H.J.H. Fenton, J. Chem. Soc. 65 (1894) 899.

[7] H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, J. Chem. Soc. Trans. 65 (1894) 899-910.

[8] Lata, H., Garg, V.K., Gupta, R.K., 2008. Desalination 219, 250-261. Li, Y.S., 1999. Waste Manage. 19, 495-502.

[9] Namasivayam, C., Radhika, R., Suba, S., 2001. Waste Manage. 21, 381-387.

[10] Rauf, M.A., Bukallah, S.B., Hamour, F.A., Nasir, A.S., 2008.

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