International Journal of Applied Chemical and Biological Sciences (2022), 3(2), 34-43
ISSN 2582-788X

RESEARCH PAPER

Article Identifier: https://identifier.visnav.in/1.0001/ijacbs-22c-03003/

Oxidative degradation of methylene blue dye from wastewater by Fenton process

Jimoh N. Jayeola *, Isah A. Bello, Fehintola A. Julius, and Sakariyau W. Adio

Department of Chemistry, Ladoke Akintola University of Science and Technology, Ogbomosho, Nigeria

* For correspondence: jayeolanurudeen177@gmail.com

Received on: 3 March 2022 *Published on: 1 April 2022*

ABSTRACT

There is something intriguing and at the same time fascinating that a simple reaction (Fe^{2+} ions with H_20_2), which was observed by H.J.H. Fenton over 110 years ago, proves to be very difficult to describe and understand. Yet the nature of oxidizing species obtained in Fenton reaction is still a subject of deliberation, which may be explained by the fact that it is very common in both chemical and biological systems in natural environment. Advance oxidation process (AOPs) show great promise for application in many wastewater treatments areas. AOPs are emerging technology that may be employed for specific goals in wastewater treatment. The Application of Advance Oxidation process (AOPs) for dyes wastewater treatment is the focus. Fenton reagents as one of AOPs were applied for the minimization of organic content of coloured synthetic wastewater. Methylene Blue (MB) Dye was used as the model organic pollutants. Fenton type process was examined in orders to established optimal operating condition (pH, Hydrogen Peroxide (H_20_2) concentration, ferrous ion catalyst concentration (Fe^{2+}) [Fe^{2+}] / [H_20_2] Fenton ratio, dye concentration and temperature for maximum degradation of the investigated simulated coloured wastewater. It was found out that optimum conditions were obtained at pH of 3, hydrogen peroxide of concentration 70mM, Iron catalyst concentration of 4mM, the Fenton ratio [Fe^{2+}] / [H_20_2] of 1: 17.5 and temperature of 45°C. Degradation of Methylene blue dye from textile wastewater using Fentons reagent is very promising since the system achieved high reaction yield, compared to other and there is no needs for special treatment.

Keywords: Wastewater, Color Degradation, Fenton Process, Methylene Blue Dye, Fenton Reagent

1. INTRODUCTION

Extensive air and water pollution has plagued the planet for a long time. The humankind has been expediting its efforts in pollution abatement. Several approaches are used: to utilize environmentally benign processes, to provide in-situ destruction of pollutants during the process, and to decontaminate the air or water stream emanating from the high throughout production facility. The treatment of industrial wastewater before discharge to prevent the quality of natural water body from deterioration and to meet regulatory requirements continues to be a significant challenge of environmental protection. In the field of wastewater treatment, many kinds of technologies in the areas of chemistry, physics, and even biochemistry have been applied under the considerations of economics and practicability. Recently, considerable interest has been shown by researchers all over the world in the application of Advanced Oxidation Processes (AOP's) for the destruction of organic and inorganic contaminants in aqueous streams. Many literatures have reported that a lot of toxic or hazardous industrial chemicals could be destroyed by this novel technique. However, even faster decomposition is needed to carry out the oxidation at the commercial level, and in some cases, more toxic intermediates are produced during the degradation of parent chemicals.

The treatment of spent dye wastewater effluent is a growing concern for the textile industry because of aesthetic conditions, as well as eco toxicological issues regarding colored rinsing and process wastewater and the impact of that wastewater on the receiving streams. As regulations become more stringent, the effectiveness and cost of treatment processes becomes more significant. Conventional biological treatment can be ineffective for color removal, but chemical oxidative processes seem to provide an opportunity for future use in industrial wastewater. The concept behind an AOP is that exposure of a strong oxidizing agent exposed to UV light generates hydroxyl free radicals which are even stronger oxidants [1]. Color reduction in textile wastewater is measured in terms of absorbance by UV-VIS Spectrophotometer. Two other analyses commonly used for the analysis of wastewaters are total organic carbon (TOC) and chemical oxygen demand (COD), neither of which is specific for determining color reduction. A reduction in color level following the addition of an oxidant can occur either by degradation or alteration of the conjugated system of the dyes with the potential to create even more toxic chemicals in the effluent [2]. The toxicity associated with color degradation will prove to be an important factor in the choice between oxidative treatments. Previous research into the decolourization of dyes and spent textile dye effluent by chemical oxidation appeared to focus on specific dye decomposition (rates and kinetic models), initial dye concentrations, and hydrogen peroxide concentrations, and UV intensity with different contact times as important factors affecting color reduction.

This project is designed to investigate the potential of Fenton reagent for the degradation of Methylene blue as model thiazine dye compound. The specific objectives are (i) to determine the effects of pH, H_2O_2 dose, Ferrous dose, Fenton (H_2O_2 +$FeSO_4$); Fenton ratio (H_2O_2; $FeSO_4$), temperature and initial Methylene blue concentration on degradation efficiency and their optimization, (ii) to calculate the decolourization efficiency under different reaction conditions.

2. METHOD AND MATERIALS

2.1. Preparation of Solution

2.1.1. Dye solutions

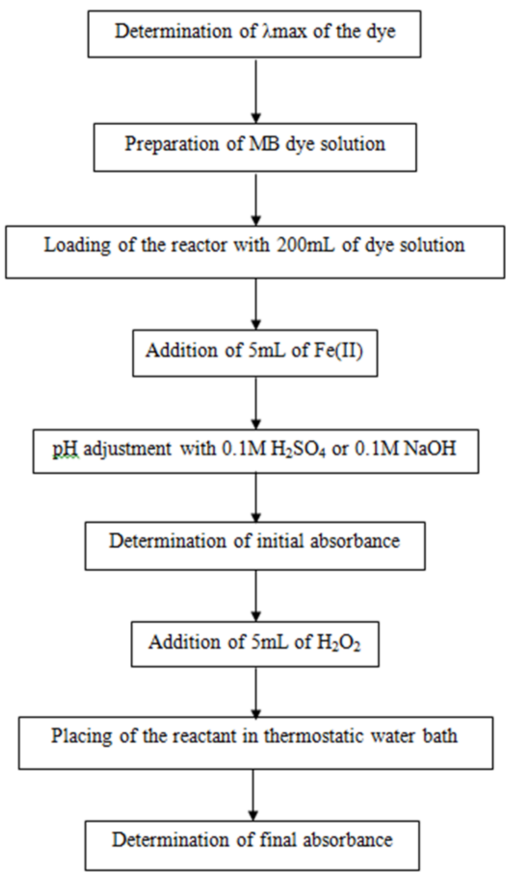
The dye solutions were prepared by dissolving a known amount of dye in distilled water, followed by quantitative transfer of the resulting dye solutions into 1000mL standard flask before filling to the mark with distilled water. The flasks were covered with aluminum foil to avoid degradation by laboratory fluorescent lights. For most of the experiments, dye solutions of 20ppm concentration were prepared by dissolving 0.02g in distilled water and making the solution quantity to 1L.

2.1.2. Hydrogen peroxide

Concentrations of hydrogen peroxide (30%w/v) ranging from 10mM-80mM were prepared from the stock solution using dilution law. Preparing 30mM of hydrogen peroxide solution 3.4mL of the stock solution was accurately measured and transferred to the1000mL standard flask and then filled to the mark with distilled water.

2.1.3. Ferrous sulphate hydrated ($FeSO_4.7H_2O$)

Experimental Flow Chart for Fenton Process



It was prepared by dissolving requisite quantity of the salt in distilled water, followed by quantitative transfer into 1000mL concentrations of the catalyst was varied within the range of 2-6mM.

2.2. *Degradation Experiment*

The reactor was initially loaded with 200mL of MB aqueous solution, adding 5mL of ferrous catalyst, following by adjusting the pH value. Continuous mixing was maintained by means of magnetic stirrer. The reaction was initiated by adding 5mL of H_2O_2 and the time was recorded. The reaction was terminated by adding 0.5mL of 10M NaOH [3]. The degradation of methylene blue dye was carried out in batch operation. Temperature was controlled through a thermostat. Experiments were performed in triplicate and results were given as the mean values.

2.3. *Efficiency of the Colour Degradation*

The efficiency of the colour degradation is expressed as percentage ratio of the decolourized dye absorbance to that of initial one [4-5].

$$\text{Colour degradation percentage} = \frac{A_0 - A_t}{A_0} \times 100 \qquad ...eq.\ 1$$

Where,
A_0= initial absorbance at 664nm,
A_t=absorbance of the dye at reaction time t (mins) at 664nm.

3. RESULTS AND DISCUSSION

The effectiveness of various oxidative treatments for reducing colour in methylene blue dye solution was evaluated in batch reactors at specific temperatures. A matrix of experimental variables was developed in which the pH, H_2O_2 concentration, $FeSO_4.7H_2O$ concentration were varied and applied to the simulated textile waste water dye solution. The goal was to evaluate the best effective treatment i.e Fenton Reagent for reducing the colour of methylene blue (MB) thiazine dye solution used in textile dyeing operations and other areas.

3.1. *Effect of pH on Fenton process*

Fenton oxidation is known as a highly pH dependent process since pH plays important role in the mechanism of HO generation in Fenton reaction. The hydroxyl radicals can be efficiently formed under acidic conditions [6]. To find the optimum pH for maximum degradation of MB dye solution, a series of experiments were conducted at different pH values in the range of 2-7 by adding either H_2SO_4 or NaOH. The effect of pH on decolourization of MB dyes by Fenton process (figure 1). This figure shows that pH significantly influences the dye degradation. At pH more than 5, as evident from the figure, a very low colour degradation of less than 10% was produced. At high pH, ferrous ions are unstable and they would easily form ferric ions which have tendency to produce a colloidal ferric hydroxo complex. The production of HO• gets slower because of the formation

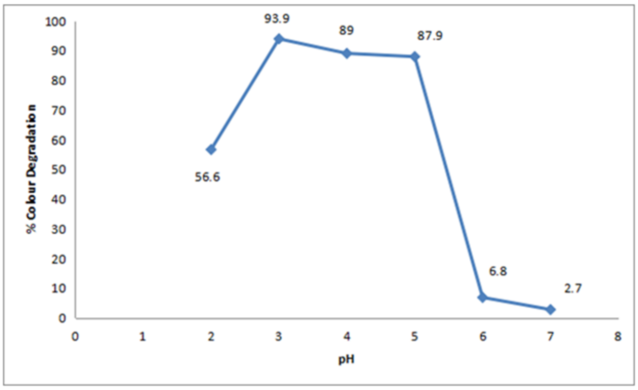


Figure 1. Effect of pH on degradation percentage of MB dye. Operating conditions: $[H_2O_2]$ =7 0mM [Fe2+] = 4mM, reaction time=60mins, [MB] =20ppm, T=25°C

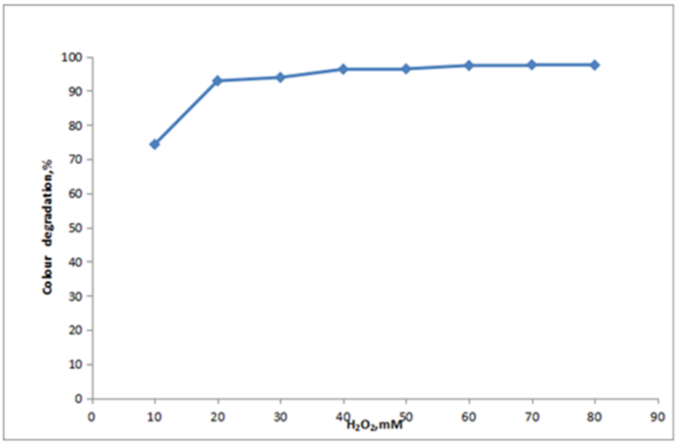


Figure 2. Effect of H_2O_2 dose on degradation percentage of MB dye. Operating conditions: pH=3, [Fe2+] = 4mM, reaction time=60mins, [MB] =20ppm, T=25°C

of this species which impeded further reaction of Fe^{2+} and H_2O_2 .At a pH of 3-5, the degradation percentage obtained was greater than 80%. Under these conditions, sufficient HO• are produced and Fe^{2+} is still highly soluble in water at pH 2-5 [7]. In this study, the highest colour removal was achieved at pH 3, where degradation was 93.9% for 60 minutes. However when the pH was dropped to 2, a substantial decrease in degradation efficiency was observed compared to that of pH 3. At pH 2, the degradation percentage was 56.6%.This occurrence could be explained by the high excess of hydrogen ions, behaving as an HO• radical's scavenger according to the reaction scheme (eq. 2).

$$HO\bullet + H^+ + e^- \rightarrow H_20 \qquad \text{...eq. 2}$$

The initial pH value has to be in acidic range to generate the maximum amount of HO•. Besides, the hydrogen peroxide and ferrous ion are more stable in low pH. Therefore, in order to attain a high degradation of dyes, further experiments in this study were conducted at pH of 3.

3.2. Effect of H_2O_2 Dose alone

Hydrogen peroxide plays the important role as an oxidizing agent. To make Fenton process competitive with other processes, it is necessary that the applications represent a low cost operation, which basically implies that a better control of H_2O_2 dosage. The objective of this test was to select the best operational dosage of H_2O_2 in Fenton process. The effect of H_2O_2 concentration on

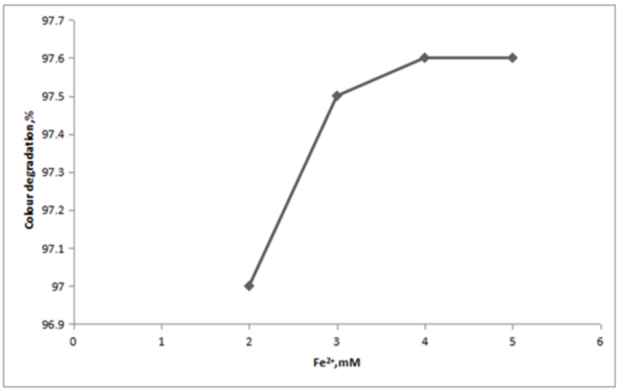


Figure 3. Effect of Fe2+ concentration on degradation percentage of MB dye. Operating conditions: pH=3, $[H_2O_2]$ = 70mM, reaction time=60mins, [MB] =20ppm, T=25°C

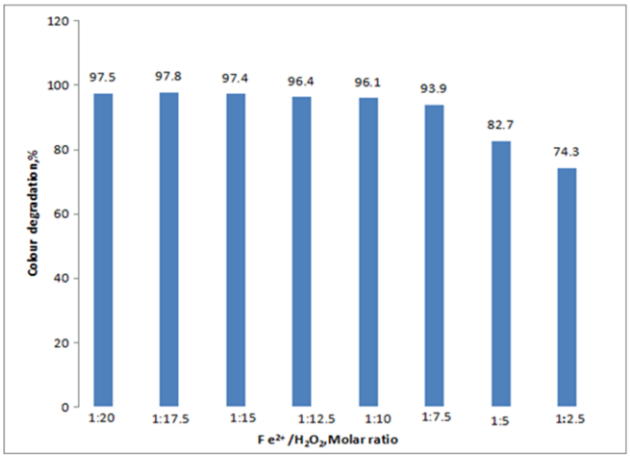


Figure 4. Effect of [Fe2+]/ $[H_2O_2]$ ratio on degradation percentage of MB dye. Operating conditions: pH=3, [Fe2+] = 4mM, reaction time=60mins, [MB] =20ppm, T=25°C

Fenton's treatment was investigated in a H_2O_2 concentration range between 10mM and 80mM, while keeping the ferrous ion dose, pH, and temperature constant at 4mM, 3 and 25°C respectively. Figure 2 shows the relationship between degradation efficiency of the dye and the concentration of H_2O_2 in Fenton process.

The results indicated that the degradation efficiency increased from 74.3 to 96.3% with increase in H_2O_2 concentration from 10mM to 30mM for 60 minutes of reaction. The increase in colour degradation efficiency was due to increase in hydroxyl radical concentration by addition of H_2O_2. Further increase from 30mM to 40mM caused no significant change in colour degradation, as it only improved by 0.1%. Doubling the concentration of H_2O_2 to 80mM only improved the efficiency by 1.2%. The highest degradation efficiency of 97.6% was achieved with 70mM H_2O_2 dose which was 0.1% higher than that obtained at 80mM of H_2O_2 dose. This little difference was due to the fact that at a higher H_2O_2 concentration scavenging of HO• will take place, which can be expressed by the equation of reaction in scheme (eq. 3).

$$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad \text{...eq.3}$$

The result is the formation of per hydroxyl radicals which are significantly less reactive than hydroxyl radicals and thus influence the degradation of the dye [8].

3.3. Effect of Ferrous Dose Alone

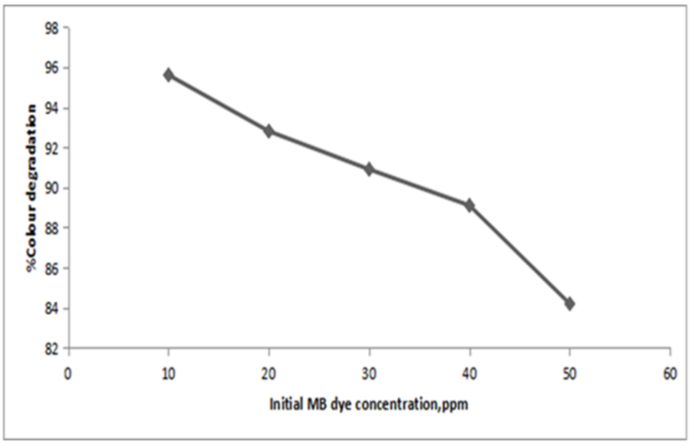


Figure 5. Effect of dye concentration on degradation percentage of MB dye. Operating conditions: [Fe2+] = 4mM, [H_2O_2] =70MM, pH=3, reaction time=60mins, T=25°C

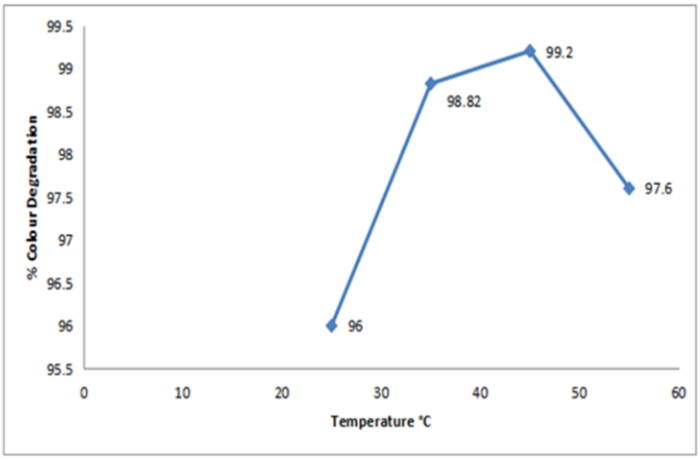


Figure 6. Effect of temperature, [Fe2+] =4mM, [H_2O_2] =70mM, pH=3 reaction time=60mins

The amount of ferrous ion is one of the main parameters influencing the Fenton process. In general, advanced oxidation of organic compounds is fast when ferrous ion is present at concentration varying between 2 and 5mM, e.g, a concentration range where sufficient HO• are produced and Fe^{2+} is still highly soluble in water at pH 2-5 [7]. Iron solubility is one of the obvious aspects in Fenton oxidation because the rate of hydroxyl radical formation is directly proportional to Fe^{2+} concentration. The effect of the addition of Fe^{2+} was studied. Different doses of ferrous catalyst from 2 to 5mM were tested (figure 3), there was no remarkable difference in degradation efficiency with increasing ferrous concentrations. The addition of Fe^{2+} from 2mM to 4mM raised colour removal from 97.0% to 97.6 %. But at 4mM to 5mM, colour degradation remained constant with further increase of Fe^{2+} concentrations. The lower degradation capacity of Fe^{2+} at small concentration was probably due to the lower HO• radical production available for oxidation. On the other hand, the excess of Fe^{2+} may scavenge the formed hydroxyl radical, which could decrease the colour degradation (eq. 4).

$$HO\bullet + Fe^{2+} \rightarrow HO^{-} + Fe^{3+} \quad ...eq.4$$

The results obtained were in line with the literature report, with increasing ferrous salt concentration, degradation rate of organic compound increases but only to that level where further addition of iron becomes insignificant [9]. The concentration of Fe^{2+} 4mM or 5mM can be used as an optimum dosage within this treatment.

3.4. Effect of Fenton ratio

Both, the ferrous ion (Fe^{2+}) and H_2O_2 not only react to form hydroxyl radicals but are also scavengers of hydroxyl radicals by reactions (eq. 4 and 5).

$$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad \text{...eq. 5}$$

The ratio of $[Fe^{2+}]/[H_2O_2]$ should affect the rates of hydroxyl radical production and scavenging. Hence it is important to use optimum $[Fe^{2+}]/[H_2O_2]$. To observe the optimal initial concentration ratio of $[Fe^{2+}]/[H_2O_2]$ on the degradation of MB dye, the fixed concentration of 4mM of ferrous ion and 20ppm of the dye were studied at varying hydrogen peroxide to give molar ratios 1:2.5-1:20.

In this study, it is clear that the best molar ratio is at the value 1:17.5 (figure 4). The results were in close agreement with other studies using Fenton treatment on the degradation of azo reactive dyes which found that the effective condition was established at iron-to–hydrogen peroxide of 1:20 [6].

3.5. Effect of the Initial Dye concentration

Pollutant concentration is an important parameter in wastewater treatment, so to study the effect of initial MB dye concentration on its degradation, the concentration range of 10-50 ppm of MB dye was investigated (figure 5). From the figure above it is evident that the percentage colour degradation decreases with increasing dye concentration. Increasing the dye concentration of MB from 10 to 50ppm decreases the colour degradation from 95.6% to 84.2% after 60 minutes of reaction. The degradation efficiencies were 95.6% (10ppm), 92.8% (20ppm), 90.9% (30ppm), 89.1 % (40ppm) and 84.2 % (50ppm) after 60 minutes of reaction time.

The increase in dye concentration increases the number of dye molecules and not HO• radical concentration and so the removal ability decreases.

3.6. Effect of Temperature

As a practical matter most commercial applications of Fenton Reagent occur at temperature between 20-40 °C. A temperature range of 25-55 °C was studied in order to investigate the effect of temperature in the Fenton treatment and the results (figure 6). The color removal increases with increasing temperature. The results indicated that raising temperature from 25 to 45 °C has a positive effect on the methylene blue (MB) dye degradation.

At 45 °C, the color degradation was 99.2%. Further increase in the temperature of 10 °C caused a slight decrease in color degradation from 99.2% to 97.6%. In the study optimal temperature of 45 °C was detected in the degradation of MB dye as opposed to some literature report [10-11] in which 30 °C was stated as optimal temperature for Fenton oxidation. Another optimal temperature 50 °C was reported on decolourization of some dyes by Fenton like reaction [12]. However observation in this study was in agreement with the finding of Dutta *et al*., (2001) who stated that there was no significant difference in the extent of color degradation in the temperature between 40°C-55°C [13]. Although from the literature there were conflicting reports as regards optimal temperatures, what is common in them that removal efficiency declined above the optimal value due to hydrogen peroxide decomposition into oxygen and water being very significant at temperature above 40°C-55°C.

Perez *et al*., (2002) worked on Fenton and Photo-Fenton oxidation of textile effluents [14]. The simultaneous use of Fenton reagent and irradiation for the treatment of textile wastewater generated during hydrogen peroxide bleaching process is investigated. The experimental conditions tested during this study provide the simultaneous occurrence of Fenton, Fenton-like and Photo-Fenton reactions. The batch experimental results are assessed in term of total organic carbon reduction. Identification of some of the chemical constituents of the effluent was performed by means of GC-MS. Other pollution related features of the initial effluent like COD and colour were also measured. The main parameters that govern the complex reactive system i.e light intensity, temperature, pH, Fe(II) and H_2O_2 initial concentrations have been studied. Concentration of Fe(II) between 0 and 400ppm and H_2O_2 between 0 and 10,000ppm were used. Temperature above 25 °C and up to 70 °C shows a beneficial effect on organic load reduction. A set of experiments was conducted under different light source with the aim to ensure the Fenton reaction has been proved to be highly effective for the treatment of such a type of waste water and several advantages for the technique application arise-from the study.

Neamtu Mariana *et al.,* (2003) worked oxidation of commercial reaction azo dye aqueous solutions by the Photo and Fenton like processes by evaluating the degradation of two azo reactive dyes, C.I reactive yellow 84 (RY84) and C.I reactive Red 120 (RR120) by Photo-Fenton and Fenton-like oxidation [6]. All experiments were performed on a laboratory scale set-up. The effect of different reaction parameters such as initial pH, contact time, effect of light and hydrogen peroxide concentration on the oxidation of the dye aqueous solution have been assessed. Effective system conditions were found to be pH of 3, H_20_2/Fe molar ratio of 20:1 and UV or solar irradiation. The colour removal efficiency at the optimum conditions during different Fenton-like processes was also evaluated. The toxic potential of the dye's degradation was investigated by the bioluminescence text using the LUMIstox 300 instrument and result were expressed as the percentage inhibition of the luminescence of the bacteria vibno fisher.

Kavethav *et al.,* (2004) worked on the role of ferrous in Fenton and Photo-Fenton processes for the degradation of phenol [15]. The efficiency of different Fenton-related oxidative process such as Fenton, solar-Fenton and UV-Fenton were examined using phenol as a model compound in simulated and industrial wastewater. A study was conducted to optimize parameter like pH, hydrogen peroxide concentration and ferrous ion concentration governing the Fenton process. At optimum conditions, different Fenton-related process were compared for the degradation of phenol. Increased degradation and mineralization efficiency were observed in photo-Fenton process. The maximum mineralizing efficiency for the phenol with Fenton, solar and UV-Fenton processes were 41%, 96% and 97% respectively. In Fenton process, carboxylic acid 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 120mm of the reaction time. In photo-Fenton processes (solar and UV light) complete degradation were observed with 0.4mM of Fe^{2+} catalyst as compared to 0.8MM of Fe^{2+} in conventional Fenton process. In Fenton and solar Fenton processes, an iron reusability study performed to minimize to the amount of iron used in treatment process. The efficacy of Fenton and solar-Fenton processes was applied to effluent from phenol resin-manufacturing unit for the removal and mineralization of pH.

4. CONCLUSION

The degradation of Methylene blue (MB) dye aqueous solution strongly depends on the system parameters such as pH, hydrogen peroxide concentration (H_2O_2), iron catalyst concentration, iron catalyst/H2O2 ratio (Fenton ratio), dye concentration and temperature. It was found out that optimum conditions were obtained at pH of 3, hydrogen peroxide of 70Mm, iron catalyst concentration of 4Mm, the [Fe^{2+}]/ [H_2O_2] ratio of 1:17.5 and temperature of 45 °C.

Degradation of Methylene blue dye from textile wastewater using Fenton process is very promising since the system achieved high reaction yield, offers a cost-effective source of hydroxyl radical. It is very simple because the chemical is readily available at a low cost and there is no need for special treatment. The removal of Methylene blue dye from textile wastewater using Fenton reagent can be scaled up for used in industry. The coming set should try and determine the percentage removal of COD using Fenton process.

5. ACKNOWLEDGEMENT

NA

6. CONFLICT OF INTEREST

The authors have declared that there is no conflict of interest.

7. SOURCE/S OF FUNDING

NA

8. REFERENCES

1. Ince, N.H and Gonenc. D.T., (1997), Treatability of a textile Azo dye by UV/H202 Environmental Technology. **18**:179- 185
2. Yang, Y., Wyatt, I. I., Travis, D., & Bahorsky, M. (1998). Decolorization of Dyes Using UV/H_2O_2 Photochemical Oxidation. *Textile Chemist & Colorist*, **30*(4)***.
3. Xu, X. R., Li, H. B., Wang, W. H., & Gu, J. D. (2004). Degradation of dyes in aqueous solutions by the Fenton process. *Chemosphere*, **57*(7)***: 595-600.
4. Meriç, S., Kaptan, D., & Ölmez, T. (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere*, **54*(3)***: 435-441.
5. Bello I.A, Giwa A.A, Aderinto O.S, Olabintan A. (2013). Effect of position of substituent on the exhaustion and thermodynamics parameters of 6 monoazo acid and dispersed dye on nylon 6. *Chem Res*: 6-11.
6. Neamtu, M., Yediler, A., Siminiceanu, I., & Kettrup, A. (2003). Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. *Journal of Photochemistry and Photobiology A: Chemistry*, **161*(1)***: 87-93.
7. Arslan-Alaton, I., Gursoy, B. H., & Schmidt, J. E. (2008). Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes. *Dyes and Pigments*, **78*(2)***: 117-130.
8. Bergendahl, J and J. O Shavghnessy, (2004). "Advance oxidation processes for Wastewater treatments" Journal of the New England Water Environment Association, in press.
9. Tarr M, (2003). Fenton and modified Fenton methods for pollutant degradation, in chemical degradation methods for waste and pollutants: CRC Press.
10. Ramirez, J. H., Costa, C. A., & Madeira, L. M. (2005). Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. *Catalysis Today*, **107**: 68-76.
11. Von Gunten, U., & Hoigne, J. (1994). Bromate formation during ozonization of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. *Environmental science & technology*, **28*(7)***: 1234-1242.
12. Medien, H. A., & Khalil, S. M. (2010). Kinetics of the oxidative decolorization of some organic dyes utilizing Fenton-like reaction in water.

Journal of King Saud University-Science, **22*(3)***: 147-153.

13. Dutta, K., Mukhopadhyay, S., Bhattacharjee, S., & Chaudhuri, B. (2001). Chemical oxidation of methylene blue using a Fenton-like reaction. *Journal of hazardous materials*, **84*(1)***: 57-71.
14. Pérez, M., Torrades, F., Domènech, X., & Peral, J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water research*, **36*(11):*** 2703-2710.
15. Kavitha, V., & Palanivelu, K. (2005). Destruction of cresols by Fenton oxidation process. *Water Research*, **39*(13)***: 3062-3072.